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THE VIBRATION SPECTRUM OF A CRYSTAL LATTICE

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1. Introduction

It is a fundamental problem in the physics of the solid state to determine the possible modes and frequencies of vibration of the atomic nucleii in a crystal about their positions of equilibrium. The importance of the problem will be evident when we recollect that there is scarcely any physical property of a solid which is not influenced in greater or less measure by the thermal agitation of the atoms, and that the existence of atomic vibrations (excited thermally or otherwise) comes into evidence in a variety of phenomena exhibited by crystals. We may, in particular, mention various optical effects observed with crystals, *e.g.*, the scattering of light with altered frequency, luminescence and absorption spectra at low temperatures, which not only render the existence of atomic vibrations in them obvious, but also enable us to make precise determinations of their vibration frequencies, and even infer their geometric characters.

An appropriate starting point for the inquiry is furnished by the well-known result in analytical mechanics that all the possible small vibrations of a conservative dynamical system about a position of stable equilibrium may be represented as a superposition of certain modes of vibration designated as the normal modes of the system. In each such mode, the particles of the system execute harmonic vibrations with a common frequency characteristic of the mode, and all pass simultaneously through their positions of equilibrium at some particular phase of the vibration. The question arises for investigation, does the structure of a crystal possess any normal modes of vibration as thus defined, and if so, what are their frequencies? In seeking an answer to this question, it is obviously not permissible to make in advance any arbitrary postulate regarding the nature of the normal vibrations, since this is itself the subject-matter of the investigation. Further, it is essential that we assume the most general type of interaction possible between the atoms in the crystal which is consistent with its known structure and symmetry properties. Indeed, in an investigation intended to

deduce results of general application, it is evidently undesirable to make any special postulates regarding the interatomic forces, *viz.*, that they are only operative as between contiguous atoms or that they are in the nature of central forces whose magnitude varies as some power of the distance. The introduction of arbitrary postulates and assumptions has indeed, as will be shown in this paper, led to misleading results in the past history of the subject.

2. *The Lagrangian Equations of Motion*

We denote the displacements of a chosen atom in a particular cell of the crystal structure from its position of equilibrium by the symbols q_{xrs}, q_{yrs}, q_{zrs}, these being parallel respectively to the three mutually perpendicular co-ordinate-axes x, y and z. Here r is an index number indicating a particular atom amongst the p atoms in the cell of the crystal structure, while s is an index number indicating the particular cell in which the atom is located. The symbols $q_{x\rho\sigma}$, $q_{y\rho\sigma}$, $q_{z\rho\sigma}$ have a similar significance, except that ρ and σ which are the atom and cell indices respectively are regarded as unspecified. The masses of the atoms are written as m_r or m_ρ.

The kinetic energy T of the vibrations of the crystal is accordingly given by the summation over all possible values of ρ and σ of the expression

$$\tfrac{1}{2} m_\rho \left[\dot{q}^2_{x\rho\sigma} + \dot{q}^2_{y\rho\sigma} + \dot{q}^2_{z\rho\sigma}\right]. \tag{1}$$

The potential energy V of the displacements of the atoms from their positions of equilibrium is given by the summation of all the terms derived from the expression

$$\tfrac{1}{2} \mathrm{K}^{y\rho\sigma}_{xrs} \cdot q_{xrs} \cdot q_{y\rho\sigma} \tag{2}$$

by making r, s, ρ, σ run over all the possible values, as also by interchanging x, y and z. The dependence of the force-constants jointly on x, r, s and y, ρ, σ is indicated by the indices attached to them. It is evident that

$$\mathrm{K}^{y\rho\sigma}_{xrs} = \mathrm{K}^{xrs}_{y\rho\sigma}. \tag{3}$$

Hence, since each distinct pair of co-ordinates appears twice over in the summation, we may replace the factor $\frac{1}{2}$ by 1 in (2), it being understood that they are written together only once. The factor $\frac{1}{2}$ is however retained for the terms which appear as the squares of the displacements.

The equation of motion which must be satisfied by any particular co-ordinate, *e.g.*, q_{xrs} is

$$\frac{d}{dt}\left(\frac{\partial \mathrm{T}}{\partial \dot{q}_{xrs}}\right) + \left(\frac{\partial \mathrm{V}}{\partial q_{xrs}}\right) = 0. \tag{4}$$

If we assume that the vibration under consideration is a normal mode for the crystal, the displacement-components of all the atoms must be of the form $q \sin \omega t$ where the q's are real quantities depending on the atom chosen

and the direction of its displacement, while ω is the same for all atoms in the crystal. On this basis, the equation for q_{xrs} becomes

$$(m_r\omega^2 - \mathrm{K}_{xrs}^{xrs})\, q_{xrs} = \sum_{y\rho\sigma} \mathrm{K}_{xrs}^{y\rho\sigma} \cdot q_{y\rho\sigma}. \tag{5}$$

The summation indicated on the right-hand side of (5) is to be understood as including the contributions due to all the displacement-components of all the atoms in the crystal with the single exception of the displacement q_{xrs} under consideration which appears on the left-hand side of the equation. There would, of course, be a whole series of equations of this type for the x, y and z displacements of every atom in the crystal, and it is necessary that all these equations are simultaneously satisfied for the given value of ω, for the vibration under consideration to possess the characters of a normal mode.

3. *The Solution of the Equations*

The clue to the discovery of the normal modes of vibration is furnished by the basic principle of crystal architecture which may be stated as follows: *A crystal consists of sets of equivalent atoms ordered in such manner that each atom in a set is both geometrically and physically related to its environment in exactly the same way as every other atom of the same set.* From this it follows that the force-constant which connects the displacements of any pair of atoms in the crystal is the same as that which connects the displacements of any other pair of atoms, provided that the two pairs of atoms can be simultaneously brought into coincidence by simple translations of the crystal lattice parallel to its axes.

Consider now the equation of motion analogous to (5) for the rth atom in a different cell, say s'. In writing it down, it is convenient to choose a running cell-index σ' different from the σ appearing in (5), but so related to it that the translations of the crystal lattice which would bring s' into coincidence with s would also bring σ' into coincidence with σ. We have then

$$(m_r\,\omega^2 - \mathrm{K}_{xrs'}^{xrs'})\, q_{xrs'} = \sum_{y\rho\sigma'} \mathrm{K}_{xrs'}^{y\rho\sigma'} \cdot q_{y\rho\sigma'}. \tag{6}$$

Now the relation between s, σ and s', σ' assumed above, taken in conjunction with the physical structure of the crystal, gives us at once the relations

$$\mathrm{K}_{xrs}^{xrs} = \mathrm{K}_{xrs'}^{xrs'} \tag{7}$$

$$\mathrm{K}_{xrs}^{y\rho\sigma} = \mathrm{K}_{xrs'}^{y\rho\sigma'} \tag{8}$$

between the force-constants appearing in (5) and (6). This identity of the force-constants appearing on both sides of the equations of motion of equivalent atoms suggests that their displacements in a normal mode of vibration

are also related to each other in a simple way. Algebraically, it is evident that if there exists between them a general relationship of the form

$$\frac{q_{xrs}}{q_{xrs'}} = \frac{q_{y\rho\sigma}}{q_{y\rho\sigma'}}, \tag{9}$$

it follows therefrom that when equation (5) is satisfied, equation (6) will also simultaneously be satisfied, and indeed also the similar equations for *all* the equivalent atoms of index r in the crystal. Further, if the general relations indicated in (9) subsist, they are sufficient to ensure that when the equations of motion of an atom of *any* chosen index number is a particular cell are satisfied, the equations of all the other equivalent atoms of the same index number in every other cell of the crystal lattice are also simultaneously satisfied; the latter is a necessary condition for the vibration to be a normal mode.

4. *Nature of the Normal Modes*

We shall now consider more closely the significance of the relations stated in (9). They may be written in the form

$$\frac{q_{y\rho\sigma}}{q_{xrs}} = \frac{q_{y\rho\sigma'}}{q_{xrs'}}. \tag{10}$$

Stated in words, the meaning of (10) is that the vibrations of the equivalent atoms in the crystal are quantitatively related to the vibrations of the other atoms forming their respective environments in an identical fashion. *Prima facie*, this is what we should expect, since equivalence of geometric position in the crystalline array of atoms necessarily involves an equivalence in the strength of the forces holding the atoms together as indicated in equations (7) and (8), and hence should result also in equivalence in respect of dynamic behaviour in a normal vibration. To make the meaning of such equivalence clearer, we may return to equation (9) and take a case in which the cells s and s' occupy contiguous positions along one of the axes of the Bravais lattice. It follows that σ and σ' would similarly occupy contiguous positions along a parallel axis. Equation (9) thus signifies that the ratio of the corresponding displacements of *any pair* of contiguous equivalent atoms in the crystal lattice is a constant characteristic of the particular axis and of the particular normal mode under consideration.

We may apply the same arguments to cells contiguous to each other respectively along the second and third axes of the Bravais lattice. The three characteristic constants thus obtained need not necessarily be the same, and we therefore devote them by α, β, γ respectively. Since the atomic displacements are real quantities and their phases in a normal mode are all either the same or opposite, the constant ratios α, β, γ must be assumed to

be *real* quantities which may be either positive or negative. If, starting from a particular cell, we move out to another which is reached by u, v, w primitive translations in the positive directions along the three axes of the Bravais lattice, the amplitude of the vibration of corresponding atoms would be altered in the ratio $\alpha^u \beta^v \gamma^w$, while if we similarly proceed in the negative direction, we would reach a cell in which the amplitudes are altered in the ratio $\alpha^{-u} \alpha^{-v} \gamma^{-w}$. Hence, if α or β or γ is numerically different from unity, we may, by proceeding sufficiently far in one direction or another from an arbitrarily chosen cell where the amplitude is small, reach cells where the amplitudes are larger than any assigned limit. Hence, the initial postulate that the vibration amplitudes are everywhere small can only be sustained if the constants α, β, γ are numerically equal to unity, and are either positive or negative. We thus obtain the result

$$\alpha = \pm 1, \ \beta = \pm 1, \ \gamma = \pm 1. \tag{11}$$

The possible choices from amongst the alternative signs in the three equations (11) are evidently independent. We have therefore *eight* possible cases, all of which are covered by the following description: *Equivalent atoms in the crystal have all the same amplitude of vibration, their phases being either the same or else opposite in successive cells of the lattice along each of its three axes.* We may also describe the position as follows: *The atomic vibrations repeat themselves exactly in a space-pattern of which the unit has twice the dimensions in each direction and therefore eight times the volume of a unit cell of the crystal lattice.* We may interpret these statements physically by considering the well-known result of coupling two exactly similar oscillators to each other, namely the appearance of two types of vibration in which the oscillators have the same phase and the opposite phases respectively. In other words, the dynamic behaviour of a crystal is a three-dimensional analogue of the case of two coupled oscillators.

5. *Enumeration and Description of the Modes*

We have now to consider the question whether the relations stated above in equation (11) uniquely determine all the possible normal modes of the atomic vibrations in a crystal. The readiest way in which we can satisfy ourselves that this is the case is by considering the question from a physical point of view. The significance of equation (11) can be stated in the following manner: *In every normal mode of vibration, the energy of the vibration is the same for every individual cell of the crystal lattice, while the amplitudes have either the same signs or else have alternately opposite signs in the successive cells.* The two parts of the proposition are complementary and taken together characterise the normal modes completely. It is easy

to see that no vibration in which either or both of these characters is departed from can be a normal mode. If, for example, the energy of the vibration were to vary from cell to cell, it would be obviously not possible for such a state of affairs to continue permanently in a homogeneous structure. Energy would be progressively transferred from the cells having the greater energy to those having less, and the nearer the cells are to each other, the more rapidly would this process occur. A normal vibration is, by definition, perfectly time-periodic and hence, the equality of the energy of vibrations in the different clles is a necessary feature of it, and this in turn is only possible if equivalent atoms have the same amplitude of vibration. It only remains therefore to consider the question of the phases. Here, again, the definition of a normal mode allows only two alternatives, namely a positive or a negative amplitude. The effect of reversing the phase of the vibration of the atom without altering its amplitude is to change the sign of the term contributed by it to the equation of motion of every atom in the crystal, leaving its magnitude unaltered. From this, it follows that equations (5) and (6) cannot be simultaneously satisfied unless all the corresponding atomic displacements have the same signs in the two equations or alternatively have all the opposite signs. These requirements are satisfied by the eight dispositions indicated by equations (11), but not by any other conceivable arrangement of positive and negative amplitudes of equal magnitude over the cells of the lattice.

The relations stated in (11) enable us to reduce the number of independent equations of the type (5) which have to be solved from an infinite set to just $3p$ equations for each of the eight distinct cases arising therefrom. The constants appearing on the left-hand side are, of course, different in each of the $3p$ equations of each set. The terms appearing on the right-hand side of each equation may be grouped into sets in which each of the $(3p-1)$ co-ordinates involved appears multiplied by what is technically an infinite series. Physical considerations, however, indicate that these series should be convergent and summable. Each of them may therefore be replaced by a single new constant. In other words, for each of the eight distinct cases arising from (8), we may frame a set of $3p$ equations connection the $3p$ co-ordinates, the constants appearing in them having new values. The solution of the sets of equations thus obtained would enable both the normal modes (*viz.*, the ratios of the atomic displacements) and the normal frequencies to be evaluated.

It thus becomes evident that the number of normal modes and normal frequencies for each of the eight cases arising from (8) is $3p$. In other words, we have $24p$ normal modes and normal frequencies, which is the

same number as the degrees of freedom of the $8p$ atoms whose vibrations form the repeating pattern in space. It should, however, be remembered that we have started from the assumption that the crystal as a whole is at rest. Its centre of gravity must therefore remain fixed, and this gives three conditions of constraint which would reduce the number of solutions by 3. Thus in all, we have only $(24p-3)$ normal modes and frequencies of vibration. The individual cell of the crystal lattice is the unit of the repeating pattern in space for $(3p-3)$ of these modes, the atoms in the cell vibrating against each other. The repeating pattern in space for the remaining $21p$ normal modes is the super-cell already considered which has twice the dimensions and eight times the volume of a unit cell of the lattice.

It is possible to give simple geometric descriptions of the eight different types of normal modes arising from equation (11). The modes described by $\alpha = 1, \beta = 1, \gamma = 1$ may be pictured as oscillations with respect of each other of the p interpenetrating Bravais lattices of atoms of which the crystal is built up. There would be $(3p-3)$ such modes, while the other 3 degrees of freedom of these lattices may be identified as simple translations of the entire crystal which we have already excluded from the scheme. The remaining $21p$ normal modes may be pictured as oscillations relative to each other of the alternate planes of equivalent atoms in the crystal. If for example, $\alpha = 1, \beta = 1$ and $\gamma = -1$, the alternate planes of the atoms containing the α and β axes and intersecting the γ axis would oscillate against each other. If $\alpha = 1, \beta = -1, \gamma = -1$, the alternate planes of atoms passing through the α axis and cutting both the β and γ axes would oscillate against each other. If α, β, γ are all negative, the oscillating planes of atoms would intersect all the three axes at the appropriate angles. In the case of a cubic crystal, for example, the oscillating planes of atoms would be those respectively parallel to the cubic, dodecahedral and octahedral faces of the crystal.

6. *Nature of the Atomic Frequency Spectrum*

The result which emerges from the foregoing discussion is that the *vibration spectrum of the crystal consists of a set of discrete monochromatic frequencies which may be described as arising from the vibrations against each other of the atoms located in the units of an* 8*-cell super-lattice.* In deducing this result, we have regarded the crystal as a three-dimensionally periodic structure infinitely extended in space, and ignored the existence of any external boundary. This procedure appears justified. For, in the equations of motion of an atom, the terms contributed by the other atoms in the crystal must necessarily be assumed to form a convergent

series, in other words, their influence on its motion reaches a limiting value when the size of the crystal is increased indefinitely. Hence, the presence or absence of an external boundary can make no sensible difference to the modes of the atomic vibrations in the interior of the crystal.

It may be remarked also that the number of discrete frequencies observable would be very considerably diminished if the crystal belongs to a class exhibiting a high type of symmetry. For, in such a case, several of the modes of vibration reckoned as distinct in the preceding enumeration would possess identical frequencies. Taking for instance a crystal of the cubic system, we recognize that the symmetry of the crystal would result in the eight distinct sets of frequencies indicated by equation (8) being in effect reduced to four. In one set of normal modes, all equivalent atoms in the crystal move in the same phase: in three sets of normal modes, the equivalent atoms so moving lie in planes parallel to one or another of the cube faces and the corresponding frequencies would therefore be the same; in three others again, planes of atoms parallel to the dodecahedral faces move in the same phase, and the corresponding frequencies will therefore be identical: in the eighth set, the planes of atoms moving in the same phase are parallel to the octahedral faces. The total number of distinct frequencies possible is thus reduced from $(24p-3)$ to $(12p-3)$. A further reduction will arise if the directions of movement of the atoms in normal modes reckoned as distinct in this enumeration are actually equivalent. For instance, the existence of a normal mode in which all the equivalent atoms oscillate parallel to one of the cube axes necessarily involves the possibility of two others having the same frequency. In these and other ways, a very considerable reduction in the number of distinct frequencies and consequent simplification of the vibration spectrum would result.

7. *Elastic Vibrations of the Crystal Lattice*

As already remarked, the $24p$ degrees of freedom of the atoms contained in the cells of the super-lattice gives us only $(24p-3)$ normal modes of atomic vibration. The 3 degrees of freedom of translation of the super-cell left over in this enumeration must therefore be assigned to modes of vibration of a different nature. The natural assumption to make is that they represent the lower frequencies of vibration coming under the general description of elastic vibrations of the crystal lattice. On this basis, the elastic vibrations represent only one-eighth of the total number of degrees of freedom in the case of crystals consisting of a single Bravais lattice, one-sixteenth of the number when there are two interpenetrating Bravais lattices, and a still smaller proportion when there are three, four or

more atoms in the unit cell, finally becoming a negligible fraction of the whole in crystals of even moderately complex structure.

According to the classical theory of elasticity, waves of any frequency and of corresponding wave-length are possible within an infinitely extended solid, but specific modes of elastic vibration can only exist in a solid of finite extension, its shape and dimensions determining the modes as well as their frequencies. As we have seen, however, an atomistic approach gives a wholly different result, *viz.*, that the normal modes and frequencies are determined by the internal structure of the crystal, the form and dimensions of the external boundary being irrelevant. The apparent contradiction between these conclusions disappears when we notice that the classical theory of elasticity describes the low-frequency region of the vibration spectrum, while the atomistic theory describes the high-frequency end. The two types of vibration differ in important respects. In the atomic vibrations properly so called, the absolute and relative atomic displacements are throughout of comparable magnitude, while in the elastic vibrations, the translatory movements of the lattice cells are greater than the relative atomic displacements approximately in the ratio of the wave-length to the cell dimensions. While the two types of vibration may possibly tend to resemble each other in a transitional range, we are not justified in extrapolating either theory into the region of frequency in which it is wholly inapplicable.

The inappropriateness of the elastic solid theory in considering the high-frequency vibrations of a crystal lattice needs to be particularly emphasised. The theory is based on the idea that the material is a continuum having a uniform density and elasticity, whereas in reality, the crystal has a discrete atomistic structure. X-ray investigations show that the electron-density in a crystal is not uniform but is a triply-periodic function of position. The Fourier components of the electron density have noteworthy amplitudes, but they fall off with increasing order rapidly. The discontinuity of crystal structure is even more striking when we consider the mass-distribution. This is concentrated at the individual lattice points occupied by the atomic nucleii, and a Fourier analysis of the density distribution would therefore give component amplitudes which do not diminish with the order and each of which would by itself be greater than the average density of the crystal (by a factor of two in the case of a single set of atomic planes). This is a state of affairs very remote indeed from the uniform mass-density and elasticity assumed in the classical theory. Hence, only when the elastic wave-lengths are large compared with the crystal spacings could we expect a concordance between the facts and the results of that theory. For smaller wave-lengths and higher frequencies, the theory must fail, as is evident

when we consider the behaviour of elastic waves in a medium exhibiting very pronounced stratifications of mass density or elasticity. If the Fourier components of space-variation of density were *small*, we would have selective reflections of the elastic waves analogous to the familiar optical or X-ray reflections by stratified media. The *large* amplitude of the Fourier components of mass-density however alters the situation radically, and it is readily shown that *the bands of selective reflection of the elastic waves would broaden so greatly as to result in a complete cut-off of the high-frequency region of the spectrum.** In the region of high frequencies, therefore, the ideas of the elastic solid theory are wholly irrelevant and inapplicable, and an atomistic approach to the theory becomes absolutely necessary.

One might, on the other hand, be tempted to carry over the atomistic approach which proves successful in the high-frequency region towards lower frequencies. To do this, one may assume that modes of vibration exist in which groups of atoms, as for example the super-cells considered earlier in the paper, oscillate within the crystal against other super-cells of the same kind, forming a repetition pattern of vibrations in which the space-unit is a giant cell having four times the dimensions and sixty-four times the volume of the unit cell of the crystal lattice. *Pro forma* equations of motion may even be framed for the oscillation of such groups and the possible solutions discussed on the same lines for the atomic vibration, giving us eight sets of possibilities of the same kind as those given by (11); one of these, namely that in which all the super-cells vibrate in the same way should be excluded, as this would involve displacements of the centre of inertia of the entire crystal. The 8×3 or 24 degrees of freedom of oscillation of the super-cells contained in the giant cell would thus give us 21 modes of vibration, leaving as before, 3 degrees of freedom to be assigned to still lower frequencies of vibration. In the case of crystals of high symmetry, the number of distinct frequencies thus arising would naturally be reduced much below the maximum of 21.

An approach of the kind suggested above is obviously lacking in rigour, since it leaves the movements of the individual atoms within the oscillating super-cells unspecified. It is however not without value, since it indicates that as we come down the scale of frequency, the vibrations in the lattice may tend to take on the character of group movements which are intermediate in character between the purely atomic vibrations occurring at the high-frequency and the purely mass movements at the low-frequency end.

* *Cf.* Scientific Papers of the late Lord Rayleigh, Vol. III, Art. 142, Equation (74); *Phil. Mag.*, 1887, **24**, 145.

The configuration of the vibrating groups bears a specific relation to the structure of the crystal instead of, as in the elastic vibrations, being determined solely by the form and dimensions of the external boundary of the crystal. It is also clear that the frequencies of the group movements would be related to the size of the groups in much the same way as the frequency of elastic waves is related to their wave-lengths. If such group oscillations exist, as seems not unlikely in the higher ranges of the elastic spectrum, the frequency distribution in the latter would tend to approach the discreteness characteristic of the atomic vibration spectrum, instead of being continuous as indicated by the classical theory of elasticity.

8. *Remarks on Some Earlier Theories*

The close analogy between the vibration-spectra of molecules and of crystals indicated by the foregoing theory receives unmistakeable support from the results of the experimental investigation of crystal spectra by the several distinct methods to which reference has been made earlier in the paper. The results of the present theory are however in striking contrast with the ideas widely prevalent at the present time regarding the nature of the atomic vibrations in crystals. It is necessary, therefore, at this stage to make some critical comments on the earlier views which have found currency in the literature of the subject.

The well-known and closely allied theories of Debye and Born on the atomic vibrations in solids were put forward about the same time (1912) in order to explain their thermal behaviour at low temperatures. As was shown earlier by Einstein in 1907, however, the frequencies of the atomic vibrations which constitute the thermal energy of a solid lie in the infra-red region of the electromagnetic spectrum. It follows that the evaluation of the specific heat of a solid must depend on a knowledge of its spectroscopic properties in the infra-red frequency region. The experimental spectroscopic data for solids available in 1912 were, however, of a very meagre description. This may have been the reason why Debye and Born sought a different path from that indicated by Einstein and endeavoured to calculate the specific heat of solids by identifying their thermal energy with the energy of elastic vibrations of all possible frequencies. However, recent spectroscopic studies with many crystals, including especially several of the simplest chemical composition, show this identification to be unjustifiable. For, *they reveal numerous characteristic or monochromatic frequencies lying in the remotest infra-red*, in other words, within just the region which was sought to be described as a continuous spectrum of elastic vibration frequencies.

Both Debye and Born assumed that the normal modes of atomic vibrations have the same relation to the external dimensions of the solid as do the vibrations of the elastic type. This assumption is not, however, a reasonable one, since the modes and frequencies of the *mass* movements involved in elastic vibration and the modes and frequencies of *atomic* vibration depend on wholly different factors. These are the macroscopic properties and dimensions of the solid for the former, while for the latter they are the individual masses of the atoms and the manner in which they are arranged and bound together in the fine structure of the crystal. The considerations already set out above indicate that the external boundary of the solid can have no determining influence either on the normal modes or the normal frequencies of the atomic vibrations. On the other hand, the size and shape of the solid is the principal factor in determining the normal modes and frequencies of its elastic vibrations.

It is thus evident that theoretical considerations and experimental facts alike compel us to reject the assumptions on which the Debye and the Born theories are based.

9. *Born's Postulate of the Cyclic Lattice*

In the Born theory, the lattice structure of the crystal is formally taken into consideration on the basis of the so-called "Postulate of the Cyclic Lattice".* This postulate assumes the *phase* of the vibration to alter progressively along each of the axes of the Bravais lattice in such manner that the "phase-wave-length" is a sub-multiple of an arbitrary chosen length which is itself a large integral multiple of the lattice spacing. Thus, for each axis, the number of possible phase-wave-lengths is equal to the number of lattice spacings contained in the given length, and when all the three axes are considered, the total number of possibilities becomes equal to the total number N of lattice cells contained in the assumed large volume of the crystal. When multiplied by 3 p (the number of degrees of freedom of motion of the atoms in each cell), the total number of possibilities is increased to 3 Np. Each of these is assumed to represent a possible normal mode of vibration with a corresponding frequency. Since the lengths of the "phase-waves" are assumed to be the various sub-multiples of an arbitrarily assumed large multiple of the lattice spacing, they bear no simple relation to the crystal spacings themselves. Indeed, the phase-wave-lengths postulated crowd up increasingly as they become smaller, and hence the vast majority of them have values *intermediate* between small integral

* *Problems of Atomic Dynamics*, by Max Born, 1926, p. 193.

multiples of the lattice spacing. It is not surprising therefore that the Born theory yields an immense array of frequencies which form a diffuse continuous spectrum and which correspond to the assumed practically infinite array of possible phase-wave-lengths.

From the statement made above regarding the Born postulate,† it will be evident that it is equivalent to taking the ratios α, β, γ considered in Section 4 of the present paper as imaginary quantities, *viz.*,

$$\alpha = e^{i\phi},\ \beta = e^{i\psi},\ \gamma = e^{i\chi}. \tag{12}$$

As already pointed out however, such an assumption would be illegitimate, since in any normal mode the phase of vibration must everywhere be either the same or the opposite, in other words, the only possible values of ϕ, ψ, χ are either o or π, making α, β, γ equal to either plus or minus unity, as indicated in our equation (11). If, on the other hand, it be suggested that equation (12) does not refer to a normal vibration but only to a "wave" in the lattice, then before it could be used for calculating the possible frequencies of atomic vibration, it would be necessary to show that the real amplitudes obtained by superposing on it another "wave" in the opposite sense given by

$$\alpha = e^{-i\phi},\ \beta = e^{-i\psi},\ \gamma = e^{-i\chi} \tag{13}$$

would satisfy the requirements for a normal vibration. The result of superposing the "waves" represented by (12) and (13) would be to give a vibration of which the amplitude is proportional to the product $\cos(\phi l_1) \cos(\psi l_2) \cos(\chi l_3)$ where l_1, l_2, l_3 are the three cell index-numbers counted respectively along the three axes. As already remarked, however, Born's phase-wave-lengths bear no simple relation to the crystal spacings, and hence the product $\cos(\phi l_1) \cos(\psi l_2) \cos(\chi l_3)$ and therefore also the energy of vibration would vary from cell to cell within the crystal. This is a state of affairs which cannot possibly exist in a normal vibration, and it follows that except when ϕ, ψ and χ are each chosen equal to o or π, the Born phase-waves do not correspond to any real or possible normal modes of vibration. Thus, it is evident that the whole immense arrays of atomic frequencies given by the Born theory are "manufactured" by his assumption of modes of vibration which are physically impossible and that they do not possess any physical meaning or significance.

The Born postulate is in the clearest contradiction with the experimental facts observed in crystals. As an illustration, we may choose the case of diamond in view of the simplicity of its structure. The unit cell of

† *Handbuch Der Physik, Zweite Auflage*, Article by Max Born and M. Goppert-Mayer, 1933, **24**/2, p. 642.

the diamond lattice contains two atoms, and the Born theory would therefore yield a continuous spectrum with two optical and two acoustic branches, and hence exhibiting (at the most) four diffuse peaks or maxima. On the other hand, according to the present theory, the atomic vibrations in the 8-cell super-lattice would have (2 x 24 − 3) or 45 modes, but on account of the high symmetry of the crystal, the number of distinct frequencies would be reduced to 8. The highest of these frequencies represents the oscillation of the two interpenetrating lattices in the crystal against each other and appears as a sharp and intense line with a frequency-shift 1332 cm.$^{-1}$ in the spectrum of the scattering of light by diamond. The remaining seven modes of lower frequency are longitudinal or transverse oscillations against each other of the planes of equivalent atoms in the crystal lying parallel to the faces of the cube and the octahedron. Several distinct methods of investigation of the lattice spectrum of diamond are available, the results of which are an independent check on each other. The spectroscopic studies of P. G. N. Nayar* show the existence of a whole series of discrete frequencies from 1332 cm.$^{-1}$ downards, and the values for these frequencies as deduced from the scattering, flourescence and absorption spectra are in complete agreement with each other. While Nayar's experimental results find a natural explanation on the theory set forth in the present paper, they are wholly irreconcilable with the Born postulate and its consequences.

10. Summary

Starting from the most general expression for the potential energy of the displacements of the atoms in a crystal from their positions of equilibrium, their normal modes of vibration are derived. It is shown that in all the possible modes, the equivalent atoms in the crystal have all the same amplitude of vibration and either the same phase or alternately opposite phases in the successive cells of the lattice along each of its three edges. The vibrations thus form a repeating pattern in space of which the unit has twice the dimensions and eight times the volume of the lattice cell. The vibration modes are closely analogous to that of a molecule with the appropriate symmetries and containing eight times the number of atoms included in the lattice cell. The spectrum thus consists of a discrete set of monochromatic frequencies, the number of which is finite and is further reduced when the crystal belongs to a highly symmetric class. The small residue of degrees of freedom not included in this description appears as quasi-elastic vibrations having specifiable low frequencies.

* P. G. N. Nayar, *Proc. Ind. Acad. Sci.*, 1942, **15**, 293.

NORMAL OSCILLATIONS OF THE DIAMOND STRUCTURE

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1. Introduction

In an earlier paper, Venkatarayudu[1] has used group theoretical methods to show that the primary normal oscillation of the diamond structure consists of a mutual displacement of the two interpenetrating lattices, the direction of displacement being arbitrary. This analysis and similar work in respect of other crystals already published by the author and Venkatarayudu[2] are based on the fundamental assumption that the smallest unit or the Bravais cell of the structure is the repeating pattern both from the static and from the dynamic points of view. That the next stage in the analysis would be to consider a super-lattice of which the cells have twice the edge length of the smallest cell and that the oscillations thus derived would have also to be reckoned in formulating the basic theory of crystal dynamics and of the thermal energy of crystalline solids was pointed out by Raman.[3] In a paper* now under publication, Raman[4] is giving a proper theoretical foundation for the idea of the super-lattice frequencies put forward by him earlier.

In this paper, group theoretical methods are applied to the case of diamond and the results appropriate to a repeating unit which has eight times the volume of the smallest unit cell are given. This repeating unit is formed by taking twice the primitive translation as the side of the cell along each direction instead of the primitive translation itself. Such a cell contains 16 carbon atoms whereas the smallest one contains only 2.

2. Diamond Structure and its Symmetry Operations

In Fig. 1 is shown a portion of the diamond structure which is made up of two interpenetrating lattices. The dark circles denote atoms belonging to one lattice whereas the white circles denote the atoms belonging to the other. The smallest unit cell is a rhombohedron formed by the primitive translations 1, 2; 1, 3 and 1, 4. Such a rhombohedron contains only two

* An advance copy of this paper has been very kindly sent by Professor Raman to the present author.

distinct atoms which are numbered 1 and 5. In such a case translations 1, 2; 1, 3 and 1, 4 cannot be regarded as distinct from the identity operation

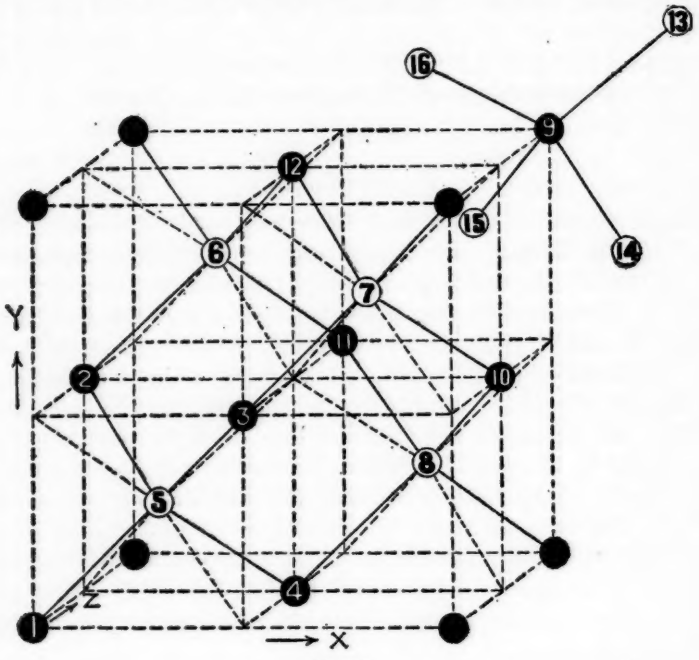

FIG. 1

and all the atoms numbered 2, 3, 4, 9, 10, 11 and 12 are equivalent to 1, whereas those numbered 6, 7, 8, 13, 14, 15 and 16 are equivalent to 5. The symmetry group will then consist of 48 elements only and has been dealt with earlier. The unit cell chosen in this paper is, however, a larger rhombohedron formed by the primitive translations which are twice 1, 2; 1, 3 and 1, 4. Such a rhombohedron contains 16 distinct atoms which are numbered 1 to 16 in Fig. 1. Besides the 48 elements of the simple group, seven translations (1, 2; 1, 3; 1, 4; 1, 9; 1, 10; 1, 11; 1, 12), which were hitherto identical with the identity element, have now to be regarded as distinct symmetry operations. These, along with the identity operation, constitute a sub-group of order 8 and the total group of symmetry operations appropriate to the diamond structure in which there are 16 non-equivalent points as shown in Fig. 1, will be formed by obtaining the product of the simple 48 elements with the above translational group consisting of 8 elements. The resulting group is of order 384. The elements of this group fall into

	E	$32C_3$	$12C_2$	12σ	$48S_4$	$4i$	$32S_6$	24σ	$24C_2$	$48C_4$	$12C_2$	$12C_2$	6T	24σ	$32C_3$	12σ	$4i$	$32S_6$	$12C_2$	T	n_i
A_1 ..	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0
A_2 ..	1	1	1	−1	−1	1	1	1	−1	−1	−1	1	1	−1	1	−1	1	1	−1	1	0
A_3 ..	1	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	1	1	1	−1	−1	−1	1	0
A_4 ..	1	1	1	−1	−1	−1	−1	−1	1	1	1	1	1	−1	1	−1	−1	−1	1	1	0
E_1 ..	2	−1	2	0	0	2	−1	2	0	0	0	2	2	0	−1	0	2	−1	0	2	0
E_2 ..	2	−1	2	0	0	−2	1	−2	0	0	0	2	2	0	−1	0	−2	1	0	2	0
F_1 ..	3	0	−1	−1	1	3	0	−1	−1	1	−1	−1	3	−1	0	−1	3	0	−1	3	0
F_2 ..	3	0	−1	1	−1	3	0	−1	1	−1	1	−1	3	1	0	1	3	0	1	3	1
F_3 ..	3	0	−1	−1	1	−3	0	1	1	−1	1	−1	3	−1	0	−1	−3	0	1	3	0
F_4 ..	3	0	−1	1	−1	−3	0	1	−1	1	−1	−1	3	1	0	1	−3	0	−1	3	1
H_1 ..	6	0	2	2	0	0	0	0	0	0	0	−2	−2	−2	0	2	0	0	0	6	1
H_2 ..	6	0	−2	0	0	0	0	0	2	0	−2	2	−2	0	0	0	0	0	−2	6	1
H_3 ..	6	0	2	−2	0	0	0	0	0	0	0	−2	−2	2	0	−2	0	0	0	6	0
H_4 ..	6	0	−2	0	0	0	0	0	−2	0	2	2	−2	0	0	0	0	0	2	6	1
K_1 ..	4	1	0	2	0	2	1	0	0	0	−2	0	0	0	−1	−2	−2	−1	2	−4	1
K_2 ..	4	1	0	−2	0	2	1	0	0	0	2	0	0	0	−1	2	−2	−1	−2	−4	0
K_3 ..	4	1	0	2	0	−2	−1	0	0	0	2	0	0	0	−1	−2	2	1	−2	−4	1
K_4 ..	4	1	0	−2	0	−2	−1	0	0	0	−2	0	0	0	−1	2	2	1	2	−4	0
M_1 ..	8	−1	0	0	0	4	−1	0	0	0	0	0	0	0	1	0	−4	1	0	−8	1
M_2 ..	8	−1	0	0	0	−4	1	0	0	0	0	0	0	0	1	0	4	−1	0	−8	1
U_R ..	16	4	4	8	2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	
$h_j\chi_j$ ..	48	0	−48	96	−96	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	

20 conjugate classes* and the appropriate character table is given here. Notation used is similar to that employed in the earlier papers of the author. The table shows that besides the translation, there are one threefold, three sixfold, two fourfold and two eightfold degenerate normal oscillations coming under various symmetry classes.

If all the last six columns and the last six rows are deleted, we get the character table containing only fourteen conjugate classes and if the number of elements in each conjugate class is properly adjusted, we get results that are appropriate to a group of 192 elements which refers to the case where the smallest cubic cell containing 8 atoms only is regarded as the repeating unit.†

3. *Normal Modes and Normal Frequencies*

Below is given one representative mode under each class. Those omitted may be written down from considerations of symmetry and taking into account the order of degeneracy in each case and the manner in which each normal co-ordinate transforms under the different symmetry operations. If the normal co-ordinates given below are read with reference to Fig. 1, it is easy to get a physical picture of each one of the modes.

$$(x_1+x_2+x_3+x_4+x_9+x_{10}+x_{11}+x_{12}) - (x_5+x_6+x_7+x_8+x_{13}+x_{14}+x_{15}+x_{16}) \quad \ldots \quad F_2$$

$$(x_1+x_2)-(x_3+x_4)+(x_9+x_{10})-(x_{11}+x_{12}) \quad \ldots \quad H_1$$

$$(x_1-x_2+x_3-x_4)+(y_5-y_6+y_7-y_8)+(x_9-x_{10}+x_{11}-x_{12}) + (y_{13}-y_{14}+y_{15}-y_{16}) \quad \ldots \quad H_2$$

$$(x_1-x_2+x_3-x_4)-(y_5-y_6+y_7-y_8)+(x_9-x_{10}+x_{11}-x_{12}) - (y_{13}-y_{14}+y_{15}-y_{16}) \quad \ldots \quad H_4$$

$$(p_2+p_3+p_4+p_6+p_7+p_8+p_9+p_{13}) - (p_1+p_5+p_{10}+p_{11}+p_{12}+p_{14}+p_{15}+p_{16}) \quad \ldots \quad K_1$$

$$(p_2+p_3+p_4-p_6-p_7-p_8+p_9-p_{13}) - (p_1-p_5+p_{10}+p_{11}+p_{12}-p_{14}-p_{15}-p_{16}) \quad \ldots \quad K_3$$

$$-(x_1-z_1)+(x_2-z_2+x_3-z_3+x_4-z_4)+(x_9-z_9) - (x_{10}-z_{10}+x_{11}-z_{11}+x_{12}-z_{12})-(x_5-z_5)+(x_6-z_6 + x_7-z_7+x_8-z_8)+(x_{13}-z_{13})-(x_{14}-z_{14}+x_{15}-z_{15} + x_{16}-z_{16}) \quad \ldots \quad M_1$$

$$-(x_1-z_1)+(x_2-z_2+x_3-z_3+x_4-z_4)+(x_9-z_9)-(x_{10}-z_{10} + x_{11}-z_{11}+x_{12}-z_{12})+(x_5-z_5)-(x_6-z_6+x_7-z_7+x_8-z_8) - (x_{13}-z_{13})+(x_{14}-z_{14}+x_{15}-z_{15}+x_{16}-z_{16}) \quad \ldots \quad M_2$$

* Writing down all the 384 elements in the form of circular permutations and classifying them into conjugate classes is a very laborious process but follows the well-known methods of group theory. Details are not given here as they would occupy much space.

† This case had been fully worked out last year by the author in collaboration with Dr. T. Venkatarayudu but the results remained unpublished.

In K_1 and K_3, p stands for a displacement x, y, z. The frequencies of these modes can be evaluated in the usual manner. Below is given a statement which shows the frequency in each case and contains a description of the corresponding normal mode.

	Mode	*Degeneracy*	$4\pi^2\nu^2$
F_2	One interpenetrating lattice oscillating against the other.	3	$\frac{8K_1}{3m} + \frac{64K_2}{3mp^2}$
H_1	Consecutive planes parallel to the cube faces of any one lattice moving along the cubic axis normal thereto in opposite directions.	6	$\frac{4K_1}{3m} + \frac{40K_2}{3mp^2} + \frac{8K_3}{m}$
H_2	Consecutive planes parallel to the cube faces of any one lattice moving transverse to the cubic axis normal thereto in opposite directions while those of the second lattice do the same thing but in phase.	6	$\frac{12K_2}{mp^2} + \frac{4K_3}{m}$
H_4	,, ,, ,, while those of the second lattice do the same thing but in opposite phase.	6	$\frac{8K_1}{3m} + \frac{4K_2}{3mp^2} + \frac{4K_3}{m}$
K_1	Consecutive planes parallel to the 111 faces of any one lattice moving along the (111) axis normal thereto in opposite directions while those of the second lattice do the same thing but in phase.	4	$\frac{2K_1}{3m} + \frac{64K_2}{3mp^2} + \frac{8K_3}{m}$
K_3	,, ,, ,, while those of the second lattice do the same thing but in opposite phase.	4	$\frac{2K_1}{m} + \frac{8K_3}{m}$
M_1	Same planes as in K_1 now move transverse to the (111) axis and hence acquire twice the degeneracy.	8	$\frac{8K_1}{3m} + \frac{34K_2}{3mp^2} + \frac{2K_3}{m}$
M_2	Same as in M_1 but planes belonging to the two lattices are in opposite phase.	8	$\frac{6K_2}{mp^2} + \frac{2K_3}{m}$

K_1 and K_3 are respectively the force constants referring to any pair of atoms which constitute the nearest neighbours and the next nearest neighbours. K_2 represents the force called into play when the angle between any two valence bonds which meet at an atom varies. p stands for the distance between a pair of nearest neighbours and is the same as the length of the valence bond.

In conclusion, the author desires to express his thanks to Sir C. V. Raman with whom he had the opportunity of discussing this subject on several occasions.

Summary

Group theoretical methods have been applied for obtaining the normal oscillations of the diamond structure on the basis of a 16 atom cell as the repeating unit. It is shown that besides the translation, there are eight normal oscillations one of which is threefold degenerate, two of which are fourfold degenerate, three of which are sixfold degenerate and two of which are eightfold degenerate. Expressions are derived for the corresponding normal frequencies by postulating suitable potential energy functions.

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THE NORMAL VIBRATIONS IN SOME TYPICAL CUBIC CRYSTALS

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1. *Introduction*

Bhagavantam and Venkatarayudu (1939) investigated the modes of atomic vibration in various crystals, employing group-theoretical methods. The starting point of their work was the proposition that the vibration-pattern repeats itself in every cell of the crystal lattice. On this basis, $(3p - 3)$ normal modes are possible, p being the number of non-equivalent atoms in the lattice cell. Crystals consisting of a single Bravais lattice, *e.g.*, various metals, would have no *discrete* frequencies of atomic vibration, while cubic crystals such as rock-salt and diamond containing two non-equivalent atoms in the cell would have only one such frequency representing a triply degenerate mode of vibration. In the introductory paper of this symposium, it has been shown, however, by Sir C. V. Raman that besides the modes considered by Bhagavantam and Venkatarayudu, there are 21 p others, and that a super-cell having twice the dimensions and eight times the volume of the unit cell of the crystal lattice is the basis of the repeating pattern of all the modes of atomic vibration except those which may properly be classified as elastic vibrations of the lattice. The complete description of these modes and the determination of their activity or inactivity in light-scattering and infra-red absorption should be possible with the aid of group-theoretical methods as applied to the atoms contained in the super-cell. The classification of the possible modes into 8 different sets characterised by different phase-relations between the successive equivalent atoms along the three axes of the Bravais lattice should considerably simplify this task. The use of the phase-relations and of the geometric description of the modes of vibration to which they lead however enables us to indicate the normal modes for crystals of not too complex a structure by quite elementary methods. Of particular importance are the cases in which the crystal possesses the symmetry of the cubic system, and the number of non-equivalent atoms in its lattice is not large, being only one, two or three.

2. *Vibrations of Face-Centred Lattices*

We shall first consider the case of the face-centred cubic lattice which is of importance in view of the fact that it forms the basis of the structure

of numerous crystals. As is well known, the unit cell of the lattice in this case is a rhombohedron, the six faces of which are parallel to the octahedral planes in the complete cubic crystal. The planes cutting the three axes of the cell at equal angles are also parallel to the faces of the octahedron. The planes which pass through one rhombohedral axis and *internally* bisect the angle between the other two axes are parallel to the dodecahedral faces, while the planes passing through one axis and *externally* bisecting the angle between the other two are parallel to the cube faces. As explained by Sir C. V. Raman in the introductory paper of the symposium, the geometric character of the atomic movements may be described in terms of these planes. The possible modes fall into one or another of the eight sets given by the relations.

$$\alpha = \pm 1,\ \beta = \pm 1,\ \gamma = \pm 1,$$

where α, β, γ are the amplitude ratios of the vibrations of successive equivalent atoms respectively along the three axes of the super-lattice cell.

The case in which α, β, γ are all positive, which we may denote by the symbol $(+\ +\ +)$, represents translations of the cell as a whole. It is thus excluded from the scheme of normal vibrations and goes over to the "elastic spectrum" of the crystal. The four cases represented by the symbols $(-\ +\ +)$, $(+\ -\ +)$, $(+\ +\ -)$ and $(-\ -\ -)$ of which the meaning should be obvious represent movements in which the *alternate* planes of atoms parallel to the *octahedral* faces oscillate against each other. Each case has three degrees of freedom associated with it, and the total of 12 degrees of freedom accordingly falls into 4 groups, each with three degrees of freedom representing different directions of movement. A *longitudinal* oscillation of the planes, *i.e.*, a movement along the trigonal axis which is their normal, clearly stands on a different footing from *transverse* oscillations of the planes. For the latter, all directions lying in the octahedral planes are clearly equivalent, and we may therefore choose any two orthogonal directions.

The cases $(-\ -\ +)$, $(+\ -\ -)$ and $(-\ +\ -)$, each with 3 degrees freedom, may be described as movements of the planes of atoms parallel to the *cube* faces. It is then easy to see that the 9 degrees of freedom associated with these modes fall into two distinct groups. In one group, the alternate planes of atoms parallel to the cube faces oscillate *longitudinally*, while in the other group they oscillate transversely. We have thus *four* distinct frequencies of vibration of the atoms contained in the super-cell; the degeneracies associated with them, together with the three translations of the super-cell total up to 24 degrees of freedom.

	Degeneracy
(1) Translations	3
(2) The octahedral planes vibrate longitudinally	4
(3) The octahedral planes vibrate transversely	8
(4) The cubic planes vibrate longitudinally..	3
(5) The cubic planes vibrate transversely	6
TOTAL ..	24

3. *The Zincblende Lattice*

In this crystal, the zinc and sulphur atoms form face-centred cubic lattices which interpenetrate each other, their relative displacement along the trigonal axis being one-fourth of the length of the body-diagonal. We have 24 × 2 or 48 degrees of freedom in all. There are four layers of atoms (alternately Zn and S) in the super-cell parallel to the octahedral and cubic planes. From the general considerations set out by Sir C. V. Raman in the introductory paper of the symposium, it follows that the oscillations of the structure are obtained by doubling up the modes derived above for a face-centred lattice, one set representing movements of the adjacent zinc and sulphur atoms in the same phases, while in the other set they are in opposite phases. We may, in fact, immediately write down the modes with *nine* distinct frequencies arising in this way, the degeneracies associated with them together with the three translations of the super-cell totalling to 48 degrees of freedom.

					Degeneracy
(1) Translations					3
(2) Oscillation of the zinc and sulphur lattices against each other					3
(3) Oscillation of the octahedral planes of atoms normally with the phases	+ Zn	+ S	− Zn	− S	4
(4) Same as (3) but with the phases ..	+ Zn	− S	− Zn	+ S	4
(5) Oscillation of the octahedral planes of atoms transversely with the phases	+ Zn	+ S	− Zn	− S	8
(6) Same as (5) but with the phases	+ Zn	− S	− Zn	+ S	8
(7) Oscillations of the cubic planes of atoms normally with the phases	+ Zn	+ S	− Zn	− S	3
(8) Same as (7) but with the phases ..	+ Zn	− S	− Zn	+ S	3
(9) Oscillation of the cubic planes tangentially with the phases	+ Zn	+ S	− Zn	− S	6
(10) Same as (9) but with the phases ..	+ Zn	− S	− Zn	+ S	6
TOTAL ..					48

4. *The Diamond Lattice*

The case is clearly similar to that of the zincblende lattice except that we have now two similar atoms instead of two dissimilar ones. There are four similar layers of carbon atoms in the super-cell parallel to the octahedral planes and also parallel to the cubic planes. The spacing of the layers parallel to the octahedral planes is alternately greater and smaller, and hence the similarity of the two atoms leaves unaffected the distinctness of the frequencies of the modes in which the layers closer to each other move respectively with the same or opposite phases. On the other hand, the four layers of atoms present in the cubic planes are equidistant, and the question therefore arises whether the movements of these planes fall into two distinct sets or merge into one. An examination of a model of a crystal shows however that in respect of oscillations in a direction *normal* to the cubic planes, all the four successive layers are symmetrically and identically circumstanced. Hence, the modes in diamond analogous to those listed as (7) and (8) for the case of zincblende have identical frequencies. On the other hand, the situation is different for oscillations *transverse* to the cubic planes. *Alternate* pairs of atoms in the planes parallel to the cubic faces appear laterally displaced with respect to each other. Hence, the modes of oscillation in which the closely adjacent layers of carbon atoms move transversely with the same or the opposite phases are quite distinct and their frequencies are different. We have accordingly the following scheme of normal vibrations for diamond, giving *eight* distinct frequencies.

		Degeneracy
(1) Translations		3
(2) Oscillation of the two interpenetrating lattices against each other		3
(3) Oscillation of the octahedral planes of atoms normally with the phases	+ + − −	4
(4) Same as (3) with the phases	+ − − +	4
(5) Oscillation of the octahedral planes of atoms transversly with the phases	+ + − −	8
(6) Same as (5) with the phases	+ − − +	8
(7) Oscillation of the cubic planes of atoms normally with the phases	+ + − − or + − − +	6
(8) Oscillation of the cubic planes of atoms transversely with the phases	+ + − −	6
(9) Same as (8) with the phases	+ − − +	6
	TOTAL	48

5. *The Rock-Salt Lattice*

Here, the sodium and chlorine ions form face-centred lattices which interpenetrate in such a manner that in the octahedral planes, the two sets of ions appear separately in alternate and equidistant layers, while in the cubic planes, they also appear in equidistant layers, but interspersed. The five sets of possibilities for the case of a face-centred lattice therefore get doubled up as in the case of zincblende, but the description of the modes would be different owing to the altered nature of the atomic arrangements. It is evident that the layers of sodium ions lying in the octahedral planes can oscillate against each other independently of the chlorine ions, and *vice versa*. On the other hand, in the cubic planes, the oscillations of the two sets of ions are necessarily coupled with each other. We have thus the following scheme for the rock-salt lattice giving *nine* distinct frequencies.

	Degeneracy
(1) Translations	3
(2) Oscillation of the sodium and chlorine lattices against each other	3
(3) Oscillation of the sodium layers against each other normally to the octahedral planes	4
(4) Oscillation of the chlorine layers against each other normally to the octahedral planes	4
(5) Same as (3) but transversely	8
(6) Same as (4) but transversely	8
(7) (*a*) } Coupled oscillation of the sodium and chlorine ions normally to the	 3
(7) (*b*) } cubic planes	3
(8) (*a*) } Coupled oscillation of the sodium and chlorine ions tangentially to the	 6
(8) (*b*) } cubic planes	6
TOTAL ..	48

6. *The Fluorspar Lattice*

The fluorite structure differs from that of zincblende and diamond in having *three* interpenetrating face-centred lattices instead of two, all the eight places within the cubic cell being occupied by the F ions instead of four being empty as in the diamond structure. We have in all 24×3 or 72 degrees of freedom, and the modes of vibration may be derived from those of a face-centred lattice by considering the three possible alternatives; (*a*) the Ca and the two F ions are all in the same phase of vibration; (*b*) the Ca ion is one phase and the two F ions in the opposite phase; and (*c*) the two F

ions move in opposite phases, the Ca ions being at rest. In the octahedral planes, the Ca and F ions appear in distinct layers at unequal intervals, each Ca layer having two F layers disposed symmetrically on either side. On the other hand, in the cubic planes, the atoms appear in equidistant layers, the Ca ion and the F ions jointly occupying the alternate layers. We have accordingly the following scheme of normal modes for the fluorite lattice, giving us fourteen distinct frequencies of vibration.

		Degeneracy
(1) Translations		3
(2) Oscillation of the Ca lattice jointly against the two F lattices		3
(3) Oscillation of the two F lattices against each other, the Ca lattice being at rest		3
(4) Oscillation of the octahedral planes normally against each other with the phases	+ + + − − − F Ca F F Ca F	4
(5) Same as (4) with the phases ..	− + − + − + F Ca F F Ca F	4
(6) Same as (4) with the phases ..	+ − − + F F F F	4
(7) Same as (4) but transversely ..	..	8
(8) Same as (5) but transversely ..	..	8
(9) Same as (6) but transversely ..	..	8
(10) Oscillation of the cubic planes normally with the phases	+ + − − Ca F_2 Ca F_2	3
(11) Same as (10) with the phases ..	+ − − + Ca F_2 Ca F_2	3
(12) Same as (10) with the phases ..	− + + − F F F F	3
(13) Same as (10) but transversely ..	..	6
(14) Same as (11) but transversely ..	..	6
(15) Same as (12) but transversely ..	..	6
	TOTAL ..	72

7. *The Vibrations of Body-Centred Lattices*

The unit rhombohedral cell in this case has its faces parallel to *three* of the dodecahedral planes of the cubic crystal, while the planes which pass through one rhombohedral axis and internally bisect the angle between the other two are also *three other* dodecahedral planes orthogonal to the first set. It follows that all the six cases (+ + −), (+ − +), (− + +),

$(+ - -)$, $(- + -)$ and $(- - +)$, each of which is associated with 3 degrees of freedom, represent movements of the planes of atoms lying in the dodecahedral planes alternately in opposite phases. There are 6 such planes, and allowing three orthogonal directions of movement in each case, a total of 18 degrees of freedom is accounted for. The three orthogonal directions of movement of the atoms lying in a dodecahedral plane are evidently (1) normal to it and parallel to a face-diagonal; (2) tangential to it and parallel to a cube-edge and (3) tangential to it and parallel to a face-diagonal, and these represent distinct cases. The case $(+ + +)$ represents translations of the super-cell, while the case $(- - -)$ represents an oscillation of all the atoms located at the cube-corners moving in the same phase against all the atoms located at the body-centres moving together in the opposite phase.

The 24 degrees of freedom of the atoms contained in the super-cell have accordingly to be grouped in the following manner, giving *four distinct* frequencies.

	Degeneracy
(1) Translations	3
(2) Oscillations of the alternate dodecahedral planes against each other normally to themselves along a face-diagonal of the cube	6
(3) Oscillations of the alternate dodecahedral planes against each other tangentially to themselves along a cube edge ..	6
(4) Oscillations of the alternate dodecahedral planes against each other tangentially along a face-diagonal of the cube..	6
(5) Oscillations of the body-centre atoms against the cube-corner atoms in any three orthogonal directions.. ..	3
TOTAL ..	24

8. *The Cæsium Chloride Lattice*

This structure consists of two simple cubic lattices interpenetrating each other in such manner that the Cs ions are located at the body-centres of the cubic lattice formed by the Cl ions and *vice versa*. As a preliminary to the discussion of this case, therefore, we have to write down the modes of vibration for a simple cubic lattice.

The following scheme of modes for a simple cubic lattice is almost self-explanatory in view of the preceding detailed consideration of the face-centred and body-centred lattices.

	Degeneracy
(1) Translations	3
(2) Cubic planes vibrating alternately in opposite phases, normally	3
(3) Same as (2) but tangentially	6
(4) Dodecahedral planes vibrating alternately in opposite phases tangentially along a cube axis	3
(5) Dodecahedral planes vibrating alternately in opposite phases along the two dodecahedral axes in the perpendicular plane	6
(6) Octahedral planes vibrating alternately in opposite phases in three orthogonal directions	3
TOTAL ..	24

The introduction of a second interpenetrating lattice will result in all these six possibilities being doubled up, corresponding respectively to the cases in which the two adjacent non-equivalent atoms vibrate in the same phase or in opposite phases. It may be remarked that in the cubic planes the Cs and the Cl ions appear alternately in distinct and equidistant layers. Accordingly, we have the following scheme of normal vibrations for the CsCl lattice.

	Degeneracy
(1) Translations	3
(2) The Cs and the Cl lattices vibrate against each other along any 3 orthogonal directions	3
(3) The Cs ions in the cubic planes vibrate against each other with alternate planes in opposite phases, normally ..	3
(4) Same as (3) but tangentially	6
(5) Movement of the chlorine layers in the alternate cubic planes against each other, normally	3
(6) Same as (5) but tangentially	6
(7) Coupled oscillations of the Cs and Cl ions in the dodecahedral planes with alternate planes	3
(8) vibrating normally in opposite phases..	3
(9) Same as (7) but tangentially	6
(10)	6
(11) Alternate Cs layers in the octahedral planes vibrating in opposite phases against each other in any three orthogonal directions	3
(12) Similar motion as above of the chlorine layers	3
TOTAL ..	48

The author wishes to record here his indebtedness to Sir C. V. Raman, Kt., F.R.S., N.L., under whose kind guidance and encouragement the above work was conducted.

Summary

The normal modes of vibration of the simple cubic, body-centred and face-centred lattices as well as of the zincblende, diamond, rock-salt, flour-spar and cæsium chloride lattices have been derived by simple geometric methods on the basis of the fundamental ideas set out by Sir C. V. Raman in the introductory paper of the symposium. It is shown that the lattices mentioned have 5, 4, 4, 9, 8, 9, 14 and 11 distinct frequencies respectively.

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MODES OF ATOMIC VIBRATION IN THE FOURTEEN BRAVAIS LATTICES

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Introduction

In the first paper in this symposium, Sir C. V. Raman has discussed the normal modes of vibration of a crystal lattice, and has come to the conclusion that. in a normal mode, the atoms in adjacent cells must vibrate either in the same or opposite phases. In other words, starting from any atom, if one proceeds to an equivalent atom in the next cell by any one of the three primitive translations, the latter atom must vibrate with a phase either the same as or opposite to that of the former. If we represent the ratio of the amplitudes of atoms in adjacent cells along the three principal directions by α, β and γ, then these can take only the values $+1$ or -1. Also, the value of α, β or γ must be the same for *all* the non-equivalent atoms in the unit cell, if the equations of motion are to be satisfied. Hence, in the general study of the vibrations of crystal lattices, we may, as a first step, apply these ideas to determine the nature of the vibrations for the fundamental Bravais lattices.

It is, no doubt, true that few crystals possess the simple Bravais lattices for their structure; but any crystal can be built out of a number of such lattices interpenetrating one another. Then, the values of α, β and γ will be the same for every one of the non-equivalent atoms in the unit cell, and the vibrations will pertain to the same type as those for the simple lattice. Obviously, each mode of the simple lattice will be split up into p modes, if there are p atoms per unit cell. These will have to be determined by making use of the condition that all the p atoms in the cell must vibrate in either the same, or opposite phases, and also that the relative phases of the atoms must be identical in every cell. But a consideration of the relative phases alone is not sufficient in a general case, and one has to take into account the force system, etc. However, in some simple cases with a relatively small number of atoms occupying special positions in the lattice, a consideration of phase relations alone may suffice to enable the modes to be described more or less completely.

It is clear that a complete description of the modes, and the determination of the corresponding frequencies is, in general, not possible unless one has a knowledge of the nature of the interatomic forces in the crystal lattice. But even in the absence of such information, the symmetry of the lattice brings about a reduction in the number of discrete modes. Thus, if the application of a symmetry operation pertaining to the lattice brings one mode into coincidence with another, then the two must have identical frequencies. Since it is only the *direction* of the axes along which α, β and γ have the prescribed values that is important, one can dispense with the translation group of the space-lattice altogether, and consider only the point-group that is located at each of the lattice points. The only symmetry operators that need be considered are those that belong to this point-group, which is a sub-group of the space-group. Hereafter, by the word " operator " will only be meant a symmetry-operator of the point-group.

The description of a normal mode by the conditions $\alpha = \pm 1$, $\beta = \pm 1$, $\gamma = \pm 1$ shows that there are eight possible types of motion in the most general case, with $3p$ degrees of freedom for each, if there are p atoms in the unit cell. Of these $24p$ degrees of freedom, 3 will represent the translation of the lattice as a whole along three directions, and the remainder $(24p - 3)$ will be the number of vibrational degrees of freedom. In the present case, p is equal to unity, and the number of distinct modes of vibration will be 21 in the general case of a lattice with no symmetry. But if the lattice has some special symmetries, then it is found that the eight types are not distinct, and that some of them may be identical. Thus, they can be classified into a lesser number of sets, where the types in any set give identical frequencies.

The directions of vibration of the three modes in each type can be found as follows. Suppose that the atoms are vibrating in a particular mode. Out of the point-group of operations which brings the lattice into self-coincidence, choose one which brings atoms of the same phase into coincidence, *for that mode.* Then, the mode of vibration after applying this symmetry operation must be the same as the one before. Hence, the directions of vibration in the two cases must either be the *same* or *equivalent.* This must be true for the whole group of symmetry-operations which brings atoms of the same phase into self-coincidence. This group of operations, which may be called the group of that type of vibration, either leaves the directions of vibration invariant, or brings them into one another. We may therefore take the following as a working rule for obtaining all the information about the directions of motion that is possible by using only considerations of symmetry:

For each type of motion, involving a particular combination of α, β, γ, determine all the symmetry operations which bring atoms of the same phase into self-coincidence. With a postulated set of directions for the vibration, find if the directions are left invariant, or brought into one another. In the former case, the vibrations are non-degenerate, but if one direction is brought into another, the vibrations in these directions have the same frequency, and if all the directions are interchanged, the vibration is triply degenerate. If, on the other hand, none of the above possibilities occurs, and a direction is brought into none of the three postulated ones, then it cannot be a direction of motion for the normal mode. Another set of directions is then postulated, and the method is repeated. In this way, not only are the directions of motion determined, but the degeneracies for the vibrations in the type are also known.

For the sake of convenient reference, we shall tabulate the directions of motion and their degeneracies when the group of the type of vibration is one of certain point-groups which will be needed in this paper. The point-groups that come in are all those of the holohedry in each system. The results tabulated here could also be checked by making use of rigorous group-theoretical methods. In the second column are shown the states to which the vibrations belong, and the number of modes coupled in each. These have been arrived at by the standard method of using character tables.

Point-group	States of the vibrations	Description of the directions of vibration
C_i ..	3 coupled in A_u	Three directions unspecifiable.
C_{2h} ..	1 in A_u and 2 coupled in B_g	One direction along the 2-fold axis, and the other two undetermined, lying in the plane perpendicular to it.
D_{2h} or V_h ..	1 in B_{1u}, 1 in B_{2u}, and 1 in B_{3u}	The three directions are orthogonal, and are along the directions of the three 2-fold axes.
D_{4h}	1 in A_{2u} and 1 in E_u	One direction along the 4-fold axis, and the other two degenerate in the perpendicular plane.
D_{3d} ..	1 in A_{2u} and 1 in E_u	One direction along the 3-fold axis, and the other two degenerate in the perpendicular plane.
D_{6h} ..	1 in A_{2u} and 1 in E_{1u}	One direction along the 6-fold axis, and the other two degenerate in the perpendicular plane.
O_h ..	1 in T_{1u}	The vibration is triply degenerate.

Using the above general methods, the modes of vibration will now be worked out for the fourteen Bravais lattices. The primitive translations will

be represented by OA, OB and OC, and α, β, γ will respectively pertain to these three directions.

1. Triclinic Lattice Γ_{tr}

This lattice has the highest symmetry of the triclinic system, *i.e.*, that of triclinic holohedry, C_i. The symmetry operations are identity 1 and inversion I. The latter only reverses the direction of the primitive translations, which however does not alter the value of α, β or γ. Hence, no two modes are identical, and there are 21 distinct modes of vibration falling into 7 types. These types can be described as the vibration of atoms in alternate crystallographic planes with opposite phases. Each has three degrees of freedom, but the direction of vibration for these cannot be specified from considerations of symmetry alone, for the group of every one of the eight types is C_i, which brings any direction into self-coincidence. The description of the modes is given below:

No.	α	β	γ	*Description*	*Number of modes*
1 to 3	+	+	+	Translation of the lattice as a whole	1, 1, 1
4 to 6	+	+	−	Vibration of atoms in alternate (001) planes with opposite phases along three unspecified directions ..	1, 1, 1
7 to 9	+	−	+	Same as (4) to (6), but of alternate (010) planes ..	1, 1, 1
10 to 12	−	+	+	Same as (4) to (6), but of alternate (100) planes ..	1, 1, 1
13 to 15	−	−	+	Same as (4) to (6), but of alternate (110) planes ..	1, 1, 1
16 to 18	−	+	−	Same as (4) to (6), but of alternate (101) planes ..	1, 1, 1
19 to 21	+	−	−	Same as (4) to (6), but of alternate (011) planes ..	1, 1, 1
21 to 24	−	−	−	Same as (4) to (6), but of alternate (111) planes ..	1, 1, 1
				Total ..	24

Number of discrete modes of vibration **21.**

2. Simple Monoclinic Lattice Γ_m

This has the highest symmetry of the monoclinic system, namely that of the point-group C_{2h}. The symmetry operators are the identity 1, $A(\pi)$, S_h and $A(\pi)\,S_h$, where $A(\pi)$ denotes a 2-fold axis along the z-axis, and S_h a horizontal reflection plane normal to it, containing the x and y axes. Two of the primitive translations OA and OB are taken in the symmetry plane along Ox and Oy respectively, and the third OC is taken perpendicular to them along Oz. Obviously, the application of every one of the symmetry operations only brings the axes into self-coincidence, or reverses their direction, neither of which alters the value of α, β or γ. Hence, here also, we have 21 distinct modes of vibration, but the directions of some of these can be specified. The group of every one of these is verified to be C_{2h}, so

that one direction is along the 2-fold axis Oz, and the other two lie in the plane xOy.

No.	α	β	γ	*Description*	*Number of modes*
1 to 3	+	+	+	Translation of the lattice as a whole	1, 1, 1
4	+	+	−	Vibration of atoms in alternate (001) planes with opposite phases, normally to the planes	1
5, 6	+	+	−	Same as (4), but transversely in two undetermined directions in the plane	1, 1
7 to 9	+	−	+	Vibration of atoms in alternate (010) planes along three directions, one parallel to Oz and the other two in the plane xOy	1, 1, 1
10 to 12	−	+	+	Same as (7) to (9), but of (100) planes	1, 1, 1
13 to 15	−	−	+	Same as (7) to (9), but of (110) planes	1, 1, 1
16 to 18	−	+	−	Same as (7) to (9), but of (101) planes	1, 1, 1
19 to 21	+	−	−	Same as (7) to (9), but of (011) planes	1, 1, 1
22 to 24	−	−	−	Same as (7) to (9), but of (111) planes	1, 1, 1
				Total ..	24

Number of distinct modes of vibration **21.**

3. *Side-Centred Monoclinic Lattice* Γ_m'

In this lattice two opposite sides have atoms at the centre in addition to Γ_m. The primitive translations, as also the directions of the crystallographic axes are marked out in Fig. 1. This lattice has also the point-group symmetry of C_{2h}, and the application of the symmetry operations results in the following:

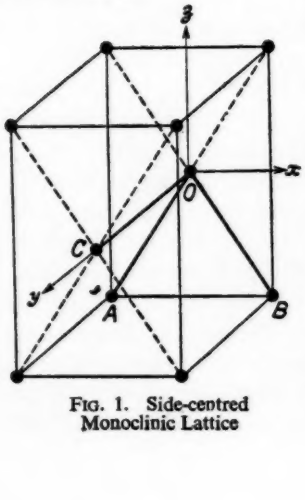

FIG. 1. Side-centred Monoclinic Lattice

1 leaves the primitive translations unaltered, and if we denote the new values of α, β, γ, by α', β', γ', respectively, then $\alpha' = \alpha$, $\beta' = \beta$, $\gamma' = \gamma$.

S_h converts OA$\rightarrow -$ OB, and OB$\rightarrow -$ OA, leaving OC unaltered. Hence, $\beta' = \alpha$, $\alpha' = \beta$, $\gamma' = \gamma$.

A (π) has the same effect on α, β, γ as S_h, and A (π) S_h produces no changes in α, β, γ.

If we work out the effect of these transformations on the eight combinations of α, β and γ, then it is found that + − + and − + + are equivalent, and that so are

$+ - -$ and $- + -$, the rest being distinct. The group of these four is only C_i so that the directions of vibration cannot be specified. For the rest, the group of the vibration is C_{2h}, and one direction is along Oz, the other two lying in xOy. The modes of vibration can, therefore, be described as follows:

No.	α β γ	*Description*	*Number of modes*
1 to 3	$+ + +$	Translation of the lattice as a whole	1, 1, 1
4 to 6	$+ + -$	Vibration of the atoms in alternate (010) planes in three directions, one along Oz, and the other two in the plane xOy	1, 1, 1
7 to 9	$- - +$	Same as (4) to (6), but of (100) planes	1, 1, 1
10 to 12	$+ - +$	Vibration of atoms in alternate $(10\bar{1})$ and (101) planes	
	$- + +$	with opposite phases in three undetermined directions	2, 2, 2
13 to 15	$+ - -$	Same as (10) to (12), but of $(11\bar{1})$ and (111) planes ..	2, 2, 2
	$- + -$		
16 to 18	$- - -$	Same as (4) to (6), but of (011) planes	1, 1, 1
		Total ..	24

Number of distinct modes **15.**

4. Simple Orthorhombic Lattice Γ_o

This lattice has the full symmetry of the orthorhombic system, *i.e.*, of the point-group V_h or D_{2h}. The symmetry operations are 1, U, V, W; S_h, US_h, VS_h, WS_h, where U, V, W are respectively rotations through π about 2-fold axes along Ox, Oy, Oz, and S_h is a reflection on the xy plane. The primitive translations may be taken along Ox, Oy and Oz, so that none of the symmetry operations alters the value of α, β or γ. Thus, for this lattice also, there are 21 modes of vibration, but the directions of the vibration can be specified for all of them, since the group of all the eight types of vibration is D_{2h}.

No.	α β γ	*Description*	*Number of modes*
1 to 3	$+ + +$	Translation of the lattice as a whole	1, 1, 1
4 to 6	$+ + -$	Vibrations of atoms in alternate (001) planes with opposite phases along the directions Ox, Oy, Oz ..	1, 1, 1
7 to 9	$+ - +$	Same as (4) to (6), but of (010) planes	1, 1, 1
10 to 12	$- + +$	Same as (4) to (6), but of (100) planes	1, 1, 1
13 to 15	$- - +$	Same as (4) to (6), but of (110) planes	1, 1, 1
16 to 18	$- + -$	Same as (4) to (6), but of (101) planes	1, 1, 1
19 to 21	$+ - -$	Same as (4) to (6), but of (011) planes	1, 1, 1
22 to 24	$- - -$	Same as (4) to (6), but of (111) planes	1, 1, 1
		Total ..	24

Number of distinct modes **21.**

5. *Side-Centred Orthorhombic Lattice* Γ_0'

This lattice has, in addition to the simple orthorhombic lattice, two points at the centres of two opposite sides. The unit cell of the lattice is shown in Fig. 2, where OA, OB, OC are the primitive translations, and Ox, Oy, Oz are the orthorhombic axes. This lattice also has the pointgroup symmetry of V_h, and the application of the symmetry operations produces the following transformations:

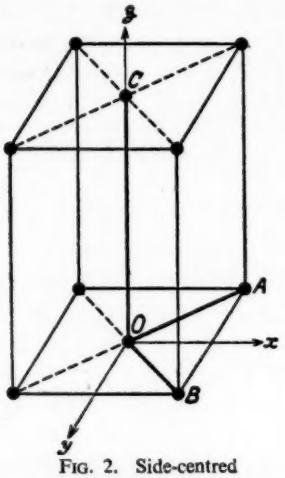

FIG. 2. Side-centred Orthorhombic Lattice

1 leaves α, β, γ unaltered.

U makes $\alpha' = \beta$, $\beta' = \alpha$, $\gamma' = \gamma$.

V makes $\alpha' = \beta$, $\beta' = \alpha$, $\gamma' = \gamma$.

W leaves α, β, γ unaltered, and S_h also does the same, so that S_h U, S_h V, S_h W have the same effect as U, V, W respectively.

Hence, out of the eight combinations of α, β and γ, only 6 are distinct, two pairs being equivalent, *viz.*, $(+ - +, - + +)$; $(+ - -, - + -)$. For these four types, the group is C_{2h}, while for the rest it is V_h. The modes of vibration can, therefore, be described as below :

No.	α	β	γ	*Description*	*Number of modes*
1 to 3	+	+	+	Translation of the lattice as a whole	1, 1, 1
4 to 6	+	+	−	Vibration of atoms in alternate (001) planes with opposite phases along the directions Ox, Oy, Oz ..	1, 1, 1
7 to 9	−	−	+	Same as (4) to (6), but of (100) planes	1, 1, 1
10 to 12	−	−	−	Same as (4) to (6), but of (101) planes	1, 1, 1
13 to 15	+	−	+	Vibration of atoms in alternate (110) and ($1\bar{1}0$) planes along three directions, one along Oz, and the other two in the plane $\perp$Oy	2, 2, 2
	−	+	+		
16 to 18	+	−	−	Same as (13) to (15), but of ($1\bar{1}1$) and (111) planes..	2, 2, 2
	−	+	−		
				Total ..	24

Number of distinct modes of vibration **15.**

6. *Body-Centred Orthorhombic Lattice* Γ_0'''

This lattice has, in addition to the simple lattice Γ_0, a point at the centre of its unit cell. The primitive translations can be taken as the line joining the centre O to three of the corners A, B, C as shown in Fig. 3. The ortho-

rhombic axes Ox, Oy, Oz will be parallel to the sides of the rectangular parallelepiped. The translation along the fourth direction OD to the adjacent atom may be represented by $(\vec{OA} + \vec{OB} + \vec{OC})$, and the phase change for the translation will be the product of those for OA, OB and OC, *i.e.*, equal to $\alpha\beta\gamma$. This lattice has also the symmetry of the point-group V_h, and the application of the symmetry operations of this group results in the following:

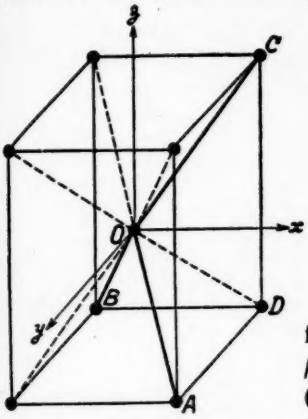

FIG. 3. Body-centred Orthorhombic Lattice

1 leaves α, β, γ unaltered.
U makes $\alpha' = \gamma$, $\beta' = \alpha\beta\gamma$, $\gamma' = \alpha$.
V makes $\alpha' = \alpha\beta\gamma$, $\beta' = \gamma$, $\gamma' = \beta$.
W makes $\alpha' = \beta$, $\beta' = \alpha$, $\gamma' = \alpha\beta\gamma$.
S_h makes $\alpha' = \beta$, $\beta' = \alpha$, $\gamma' = \alpha\beta\gamma$.
S_hU makes $\alpha' = \alpha\beta\gamma$, $\beta' = \gamma$, $\gamma' = \beta$.
S_hV makes $\alpha' = \gamma$, $\beta' = \alpha\beta\gamma$, $\gamma' = \alpha$.
S_hW makes $\alpha' = \alpha$, $\beta' = \beta$, $\gamma' = \gamma$.

On working out the effect of these transformations on the eight combinations of α, β and γ, the following sets become identical: $(+\,+\,-,\ -\,-\,+)$; $(+\,-\,+,\ -\,+\,-)$; $(+\,-\,-,\ -\,+\,+)$. For these six types, the group of the vibration is only C_{2h}, while for $(+\,+\,+)$ and $(-\,-\,-)$, it is V_h. Hence, the modes of vibration are the following:

No.	α	β	γ	*Description*	*Number of modes*
1 to 3	+	+	+	Translation of the lattice as a whole	1, 1, 1
4 to 6	−	−	−	Vibration of the two lattices, composed of the atoms at the centre, and of atoms at the corners, against one another with opposite phase, parallel to Ox, Oy and Oz	1, 1, 1
7 to 9	+	+	−	Vibration of atoms in alternate (110) and ($1\bar{1}0$) planes	
	−	−	+	along three directions, one parallel to Oz, and the other two lying in the plane xOy	2, 2, 2
10 to 12	+	−	+	Same as (7) to (9), but of (011) and ($01\bar{1}$) planes along	
	−	+	−	Ox and two other directions in yOz	2, 2. 2
13 to 15	+	−	−	Same as (7) to (9), but of (101) and ($10\bar{1}$) planes along	
	−	+	+	Oy and two other directions in zOx	2, 2, 2
				Total ..	24

Number of distinct modes **12.**

7. *Face-Centred Orthorhombic Lattice* Γ_0''

This lattice has, in addition to the simple orthorhombic lattice, atoms at the centres of the six faces. The primitive translations OA, OB, OC can be taken as the lines joining a corner to the centres of three faces intersecting at that corner, as shown in Fig. 4. The translations to the centres of the other three sides will be $(\vec{OB} - \vec{OC})$, $(\vec{OC} - \vec{OA})$ and $(\vec{OA} - \vec{OB})$, and the phase changes for these translations are $\beta\gamma$, $\gamma\alpha$ and $\alpha\beta$ respectively. Applying the symmetry operations of the point-group V_h, to which the lattice belongs, to the eight combinations of α, β, γ, we find that

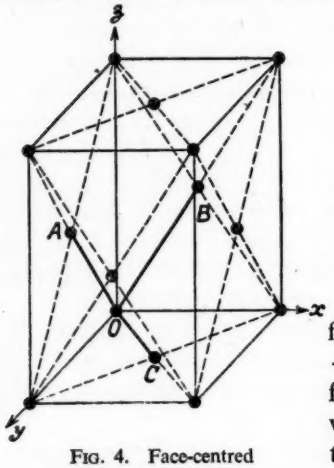

FIG. 4. Face-centred Orthorhombic Lattice

1 leaves α, β, γ unaltered.
U makes $\alpha' = \alpha$, $\beta' = \gamma\alpha$, $\gamma' = \alpha\beta$.
V makes $\alpha' = \beta\gamma$, $\beta' = \beta$, $\gamma' = \alpha\beta$.
W makes $\alpha' = \beta\gamma$, $\beta' = \gamma\alpha$, $\gamma' = \gamma$.
S_h makes $\alpha' = \beta\gamma$, $\beta' = \gamma\alpha$, $\gamma' = \gamma$.
S_hU makes $\alpha' = \beta\gamma$, $\beta' = \beta$, $\gamma' = \alpha\beta$.
S_hV makes $\alpha' = \alpha$, $\beta' = \gamma\alpha$, $\gamma' = \alpha\beta$
S_hW makes $\alpha' = \alpha$, $\beta' = \beta$, $\gamma' = \gamma$.

Working out these transformations, the following become equivalent ($+ + -$, $+ - +$, $- + +$, $- - -$), and the other four are left invariant. The group of the vibration in this set of four is only C_i, so that the directions cannot be specified. For the rest, the group is V_h, and the vibrations take place along Ox, Oy, Oz. The modes of vibration can be described as below:

No.	α β γ	*Description*	*Number of modes*
1 to 3	$+ + +$	Translation of the lattice as a whole	1, 1, 1
4 to 6	$+ - -$	Vibration of atoms in alternate (100) planes along Ox, Oy, Oz with opposite phases	1, 1, 1
7 to 9	$- + -$	Same as (4) to (6), but of (010) planes	1, 1, 1
10 to 12	$- - +$	Same as (4) to (6), but of (001) planes	1, 1, 1
13 to 15	$+ + -$	Vibrations of atoms in alternate (111), ($1\bar{1}1$), ($11\bar{1}$),	
	$+ - +$	($\bar{1}11$) planes in three unspecifiable directions ..	4, 4, 4
	$- + +$		
	$- - -$		
		Total ..	24

Total number of distinct modes **12**.

8. *Simple Tetragonal Lattice* Γ_t

This lattice possesses the full symmetry of the tetragonal system, *i.e.*, of the point-group D_{4h}. The symmetry-operations are 1, A$(\pi/2)$, A(π), A$(3\pi/2)$; U, A$(\pi/2)$U, A(π)U, A$(3\pi/2)$U; S_h, A$(\pi/2)S_h$, A$(\pi)S_h$, A$(3\pi/2)S_h$; US_h, A$(\pi/2)US_h$, A$(\pi)US_h$, A$(3\pi/2)US_h$. Here, A is a four-fold axis along Oz, and U represents a rotation through π about a twofold axis along Ox. S_h denotes a reflection in the plane xOy. We take the primitive translations along Ox, Oy, Oz respectively. Then, the application of U, A(π) and S_h does not alter the values of α, β, γ; but the operations A$(\pi/2)$ and A$(3\pi/2)$ bring about an interchange of α and β, $\alpha \rightleftarrows \beta$, leaving γ unaltered. Hence, out of the eight combinations of α, β, γ, two become equivalent with two others, *viz.*, $(+-+, -++)$; $(+--, -+-)$, and there are only six distinct sets. For the four types, $+-+$, $-++$, $+--$ and $-+-$, the group of the vibration is V_h, and the directions of vibration are distinct and lie along Ox, Oy, Oz. For the other four, the group is D_{4h}, so that one vibration is along Oz, and the other two are degenerate in the plane xOy. The modes of vibration may therefore be described as follows:

No.	α β γ	*Description*	*Number of modes*
1, 2	+ + +	Translation of the lattice as a whole	1, 2
3	+ + −	Vibration of alternate basal (001) planes normally along Oz, with opposite phases	1
4	+ + −	Same as (3), but transversely along Ox and Oy, which are, however, degenerate	2
5	+ − +	Vibration of alternate prismatic (100) and (010) planes	
	− + +	normally	2
6	+ − +	Same as (5), but transversely parallel to the tetragonal	
	− + +	axis Oz	2
7	+ − +	Same as (5), but transversely along the third perpendi-	
	− + +	cular direction, *i.e.*, Oy and Ox respectively ..	2
8	+ − −	Vibration of atoms in alternate (101), (011) planes	
	− + −	along Oz, with opposite phase	2
9, 10	+ − −	Same as (8), but along Ox and Oy	2, 2
	− + −		
11	− + −	Vibration of atoms in alternate (110) planes along the 4-fold axis Oz	1
12	− − +	Same as (11), but in two directions in the plane xOy, which are degenerate	2
13	− − −	Same as (11), but of (111) planes along Oz	1
14	− − −	Same as (11), but of (111) planes along two directions in xOy, which are degenerate	2
		Total ..	24

Number of distinct modes of vibration **12.**

9. *Body-Centred Tetragonal Lattice* Γ_t'

This lattice has, in addition to the simple lattice Γ_t, an atom at the centre of the square prism, and has the symmetry of the point-group D_{4h}. The primitive translations can be taken, as in the body-centred orthorhombic lattice, to lie along the lines joining the centre to three of the corners. In fact, Fig. 3 will suffice for this lattice, but it must be remembered that Oz is a four-fold axis in this case, and that Ox and Oy are equivalent. The effect of the symmetry operations on the primitive translations is as follows:

1 leaves α, β, γ unaltered.

A $(\pi/2)$	makes $\alpha' = \gamma$,	$\beta' = \alpha\beta\gamma$,	$\gamma' = \beta$.
A (π)	makes $\alpha' = \beta$,	$\beta' = \alpha$,	$\gamma' = \alpha\beta\gamma$.
A $(3\pi/2)$	makes $\alpha' = \alpha\beta\gamma$,	$\beta' = \gamma$,	$\gamma' = \alpha$.
U	makes $\alpha' = \gamma$,	$\beta' = \alpha\beta\gamma$,	$\gamma' = \alpha$.
A $(\pi/2)$ U	makes $\alpha' = \alpha$,	$\beta' = \beta$,	$\gamma' = \alpha\beta\gamma$.
A (π) U	makes $\alpha' = \alpha\beta\gamma$,	$\beta' = \gamma$,	$\gamma' = \beta$.
A $(3\pi/2)$ U	makes $\alpha' = \beta$,	$\beta' = \alpha$,	$\gamma' = \gamma$.
S_h	makes $\alpha' = \beta$,	$\beta' = \alpha$,	$\gamma' = \alpha\beta\gamma$.
A $(\pi/2)$ S_h	makes $\alpha' = \alpha\beta\gamma$,	$\beta' = \gamma$,	$\gamma' = \alpha$.
A (π) S_h	makes $\alpha' = \alpha$,	$\beta' = \beta$,	$\gamma' = \gamma$.
A $(3\pi/2)$ S_h	makes $\alpha' = \gamma$,	$\beta' = \alpha\beta\gamma$,	$\gamma' = \beta$.
US_h	makes $\alpha' = \alpha\beta\gamma$,	$\beta' = \gamma$,	$\gamma' = \beta$.
A $(\pi/2)$ US_h	makes $\alpha' = \beta$,	$\beta' = \alpha$,	$\gamma' = \gamma$.
A (π) US_h	makes $\alpha' = \gamma$,	$\beta' = \alpha\beta\gamma$,	$\gamma' = \alpha$.
A $(3\pi/2)$ US_h	makes $\alpha' = \alpha$,	$\beta' = \beta$,	$\gamma' = \alpha\beta\gamma$.

Using these, one finds that there are only four distinct sets, the following being equivalent $(+\,+\,-,\ -\,-\,+)$; $(+\,-\,-,\ -\,+\,+,\ +\,-\,+,\ -\,+\,-)$. Of these, only $(+\,+\,+)$ and $(-\,-\,-)$ have D_{4h} as the group of their vibration. The group of $(+\,+\,-)$ and $(-\,-\,+)$ is V_h, and of the rest, C_{2h}. Hence, the modes of vibration are as follows:

No.	α	β	γ	*Description*	*Number of modes*
1, 2	+	+	+	Translation of the lattice as a whole	1, 2
3	+	+	−	Vibration of atoms in alternate (110), $(1\bar{1}0)$ planes	
	−	−	+	normally, with opposite phase	2
4	+	+	−	Same as (3), but transversely along the tetragonal	
	−	−	+	axis, Oz	2
5	+	+	−	Same as (3), but transversely perpendicular to Oz ..	2
	−	−	+		

No.	α β γ	*Description*	*Number of modes*
6 to 8	+ − −	Vibration of atoms in alternate (011), (01$\bar{1}$) planes	
	− + +	along Ox, and two other directions in yOz, and of	
	+ − +	(101), (10$\bar{1}$) planes along Oy and two other direc-	
	− + −	tions in zOx	4, 4, 4
9	− − −	Oscillation of the two lattices composed of the atoms at the centre, and those at the corners, against one another, along Oz	1
10	− − −	Same as (9), but along two directions in xOy, which are degenerate	2
		Total ..	24

Number of distinct modes of vibration **8**.

10. *Rhombohedral Bravais Lattice* Γ_{rh}

This lattice has the full symmetry of the rhombohedral division of the hexagonal system, *i.e.*, of the point-group D_{3d}. The unit cell and the primitive translations are shown in Fig. 5, where Ox, Oy, Oz are the hexagonal crystallographic axes. The symmetry operations of the point-group D_{3d} are

1, A $(2\pi/3)$, A $(4\pi/3)$; U, A $(2\pi/3)$ U, A $(4\pi/3)$ U;
I, A $(2\pi/3)$ I, A $(4\pi/3)$ I; UI, A $(2\pi/3)$ UI, A $(4\pi/3)$ UI.

Here, A is a threefold rotation axis along 0z, U is a twofold axis along Ox, and I is the operation of inversion. Of these,

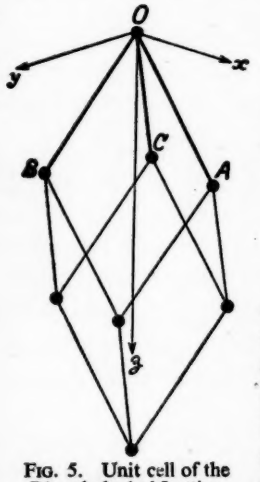

FIG. 5. Unit cell of the Rhombohedral Lattice

A $(2\pi/3)$ makes $\alpha' = \beta$, $\beta' = \gamma$, $\gamma' = \alpha$.
A $(4\pi/3)$ makes $\alpha' = \gamma$, $\beta' = \alpha$, $\gamma' = \beta$.
U makes $\alpha' = \alpha$, $\beta' = \gamma$, $\gamma' = \beta$.
A $(2\pi/3)$ U makes $\alpha' = \gamma$, $\beta' = \beta$, $\gamma' = \alpha$.
A $(4\pi/3)$ U makes $\alpha' = \beta$, $\beta' = \alpha$, $\gamma' = \gamma$.

I leaves α, β, γ unaltered, so that the other operations produce only similar transformations.

Applying these to the eight combinations of α, β, γ, one finds that they split up into four sets, (+ + +); (− − −); (+ + −, + − +, − + +); (− − +, − + −, + − −). The group of the first two sets is D_{3d}, but for the types of vibration in the other two, the group is only C_{2h}, so that the vibration is specifiable in only one direction, the other two lying in a perpendicular plane. The modes of vibration may therefore be described as follows, using rhombohedral indices.

No.	α β γ	*Description*	*Number of modes*
1, 2	+ + +	Translation of the lattice as a whole	1, 2
3	− − −	Vibration of alternate (111) planes normally along the 3-fold axis, Oz	1
4	− − −	Same as (3), but transversely, the vibration being degenerate in the plane..	2
5	− − +	Vibration of atoms in alternate $(1\bar{1}0)$, $(10\bar{1})$, $(01\bar{1})$	
	− + −	planes along the normal to the plane	3
	+ − −		
6, 7	− − +	Same as (5), but transversely in two directions in the	
	− + −	plane	3, 3
	+ − −		
8 to 10	+ + −	Same as (5) to (7), but of atoms in alternate (001),	
	+ − +	(010), (100) planes, which form the sides of the	
	− + +	rhombohedral unit cell	3, 3, 3
		Total ..	24

Number of distinct modes **8.**

11. Hexagonal Bravais Lattice Γ_h

This lattice, which is shown in Fig. 6, has the full symmetry of the hexagonal system, *i.e.*, of the point-group D_{6h}. The symmetry operations are $\{C_6\} \equiv 1$, A $(\pi/3)$, A $(2\pi/3)$, A (π), A $(4\pi/3)$, A $(5\pi/3)$, where C_6 is a sixfold axis parallel to $0z$, $\{C_6U\}$, where U is a twofold axis along Ox, $\{C_6S_h\}$ and $\{C_6US_h\}$, where S_h denotes reflection in the plane xOy. The primitive translations OA, OB, OC lie in this case along the hexagonal axes Ox, Oy, Oz respectively. The effect of symmetry operations on α, β, γ is easily seen to be as below:

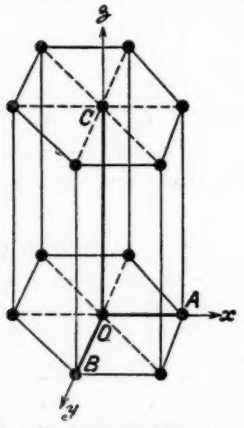

FIG. 6. Hexagonal Bravais Lattice

1 leaves α, β, γ unaltered.

A $(\pi/3)$, A $(4\pi/3)$ make $\alpha' = \alpha\beta$, $\beta' = \alpha$, $\gamma' = \gamma$.

A $(2\pi/3)$, A $(5\pi/3)$ make $\alpha' = \beta$, $\beta' = \alpha\beta$, $\gamma' = \gamma$.

A (π) makes $\alpha' = \alpha$, $\beta' = \beta$, $\gamma' = \gamma$.

U makes $\alpha' = \alpha$, $\beta' = \alpha\beta$, $\gamma' = \gamma$.

A $(\pi/3)$ U, A $(4\pi/3)$ U make $\alpha' = \beta$, $\beta' = \alpha$, $\gamma' = \gamma$.

A $(2\pi/3)$ U, A $(5\pi/3)$ U make $\alpha' = \alpha\beta$, $\beta' = \beta$, $\gamma' = \gamma$.

S_h leaves α, β, γ unaltered, so that the others need not be considered.

The combinations of α, β, γ thus reduce to the four sets (+ + +); (+ + −); (+ − −, − + −, − − −); (− − +, + − +, − + +).

For the first two types, the group of the vibration is D_{6h}, and for the others it is only V_h. The modes of vibration are, therefore,

No.	α β γ	*Description*	*Number of modes*
1, 2	+ + +	Translation of the lattice as a whole	1, 2
3	+ + −	Vibration of alternate (0001) basal planes against one another normally, along 0*z*	1
4	+ + −	Same as (3), but transversely, degenerate in the plane ..	2
5	− − +	Vibration of atoms in alternate prismatic planes $(01\bar{1}0)$,	
	+ − +	$(10\bar{1}0)$, $(1\bar{1}00)$ with opposite phases, normally to	
	− + +	the plane	3
6	− − +	Same as (5), but transversely along the hexagonal	
	+ − +	axis O*z*	3
	− + −		
7	− − +	Same as (5), but transversely perpendicular to O*z* ..	3
	+ − +		
	− + +		
8 to 10	− − −	Same as (5) to (7), but of the planes $(01\bar{1}1)$, $(10\bar{1}1)$,	
	+ − −	$(1\bar{1}01)$ planes along the same directions as in (5)	
	− + −	to (7)	3, 3, 3
		Total ..	24

Total number of distinct modes **8.**

12. Simple Cubic Lattice Γ_c

This, and the next two lattices have been discussed by E. V. Chelam in another paper appearing in this symposium. However, for the sake of completeness, and for a clearer understanding of the methods proposed in this paper, they are also tabulated. The full symmetry operations, and the detailed working will not be given here.

The simple cubic lattice has the highest symmetry of the cubic system, *i.e.*, of the point-group O_h. Taking the primitive translations along the cube axes, an application of the symmetry operations shows that the eight combinations of α, β, γ fall into four sets, $(+ + +)$; $(- - -)$; $(+ + -, + - +, - + +)$; $(- - +, - + -, + - -)$. Of these, the group of the vibrations of the type $(+ + +)$ and $(- - -)$ is O_h, so that they are triply degenerate. The group of the remaining six is D_{4h}. The modes of vibration may therefore be described as follows:

No.	α β γ	*Description*	*Number of modes*
1	+ + +	Translation of the lattice as a whole	3
2	− − −	Vibrations of alternate octahedral (111) planes with opposite phase, triply degenerate	3
3	+ + −	Vibration of alternate cube faces with opposite phase,	
	+ − +	normally	3
	− + +		
4	+ + −	Same as (3), but transversely, the vibration being	
	+ − +	degenerate in the plane	6
	− + +		
5	− − +	Vibration of atoms in alternate dodecahedral {110}	
	− + −	planes with opposite phase along the cube axis in	
	+ − −	the plane	3
6	− − +	Same as (5), but along the normal to the plane, and	
	− + −	along the third orthogonal direction, *i.e.*, the dodeca-	
	+ − −	hedral axis in the plane, the two being of the same	
		frequency	6
		Total ..	24

Number of distinct modes **5**.

13. Face-Centred Cubic Lattice Γ_c'

This lattice has points at the centres of the six cube faces in addition to those at the corners. The primitive translations may be taken as the lines joining a corner to the points at the centre of any three faces intersecting at that corner. Applying the symmetry operations of the point-group O_h to which this lattice belongs, the eight possible combinations of α, β, γ fall into three sets, (+ + +); (+ + −, + − +, − + +, − − −); (− − +, − + −, + − −). The group for the vibration in the first set is O_h, that for the second set is D_{3d} and for the third D_{4h}. The vibration in the first set is therefore triply degenerate, and in the other two, one vibration is along the threefold or fourfold axis, and two vibrations are degenerate in the perpendicular plane. The modes of vibration are as follow:

No.	α β γ	*Description*	*Number of modes*
1	+ + +	Translation of the lattice as a whole	3
2	+ − +	Vibration of alternate {111} octahedral planes with	
	+ − +	opposite phases, normally	4
	− + −		
	− − −		

No.	α β γ	*Description*	*Number of modes*
3	+ + − + − + − + + − − −	Same as (2), but transversely degenerate in the plane..	8
4	− − + − + − + − −	Vibrations of alternate {100} cube faces normally ..	3
5	− − + − + − + − −	Same as (6), but transversely the vibration being degenerate in the plane	6
		Total ..	24

Number of distinct modes **4**.

14. Body-Centred Cubic Lattice Γ_c''

This lattice has a point at the centre of the cube in addition to Γ_c, and possesses the symmetry of O_h. The primitive translations may be taken along the lines joining the centre to any three of the cube corners. An application of the symmetry operations shows that there are only three sets of combinations of α, β, γ, *viz.*, $(+ + +)$; $(- - -)$; $(+ + -, + - +, - + +, - - +, - + -, + - -)$. Except the first two, whose group is O_h, the group of all the other six types of vibration is only V_h, so that the vibrations along the three directions are of different frequencies.

No.	α β γ	*Description*	*Number of modes*
1	+ + +	Translation of the lattice as a whole	3
2	− − −	Triply degenerate vibration of the two interpenetrating cubic lattices against one another	3
3 to 5	+ + − + − + − + + − − + − + − + − −	Vibrations of alternate {110} dodecahedral planes, with opposite phases, in three directions, normally, transversely parallel to a cube axis, and transversely along the dodecahedral axis in the plane ..	6, 6, 6
		Total ..	24

Number of distinct modes **4**.

The work reported in this paper was undertaken at the suggestion of Prof. Sir C. V. Raman to whom I am extremely grateful for the many helpful discussions I had with him.

Summary

In this paper, the degeneracies and the directions of the normal modes of vibration in the fourteen Bravais lattices are worked out from symmetry considerations, making use of Sir C. V. Raman's theory. Denoting the ratio of the displacements of adjacent atoms along the primitive translations by α, β, γ, these can have only the values $+1$ or -1, so that the vibrations fall into eight types in the general case of no symmetry. In lattices possessing symmetry, however, some of the types could be brought over into others by the application of symmetry operations, and thus would be equivalent with the latter. Also, the directions of motion in any particular type of vibration may be equivalent. This is determined by selecting a group of operations which brings the atoms of the same phase to coincide for that type of vibration, and finding the directions of motion which satisfy the symmetry requirements of this group. In this way, both the directions of motion and their degeneracies are known. The number of distinct modes of vibration computed for the various lattices, are for Γ_{tr} 21; Γ_m 21, $\Gamma_{m'}$ 15; Γ_0 21, Γ_0' 15, Γ_0'' and Γ_0''' 12; Γ_t 12, Γ_t' 8; Γ_{rh} 8, Γ_h 8; Γ_c 5, Γ_c' 4, Γ_c'' 4. The modes are also described in as complete a manner as could be done by using considerations of symmetry alone.

NORMAL VIBRATIONS OF CRYSTAL LATTICES: APPLICATION OF GROUP THEORY

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1. Introduction

The usual theoretical investigations of the vibration spectra of dynamical systems (when slightly displaced from an equilibrium configuration) start with some postulated quadratic forms for the kinetic and potential energies. The problem then reduces to a transformation of the quadratic forms to sums of squares, or what amounts to the same thing, to a solution of a set of linear homogeneous equations representing the equations of motion of the system. The sets of solutions so obtained define normal vibrations which represent independent dynamical modes in each of which the system can persist for an indefinite time. In any normal vibration all the constituent atoms of the system necessarily move with the same frequency and with the same or opposite phases.

In a crystal we have to deal with an immense number of similar kinds of atoms all arranged, when in their equilibrium positions, upon a regular triply periodic structure known as the space-lattice. An actual crystal, though finite in extension is very large compared to the inter-atomic distances. When dealing with high frequency interatomic and intercellular vibrations, which obviously depend very largely upon the internal geometric arrangement of the crystal, we are clearly justified in ignoring the boundary and replacing the actual crystal by one with an infinite extension in space. This merely expresses the plausible physical assumption, that, in a crystal with an immense periodic array of atoms, all the corresponding atoms in different unit cells of the lattice stand exactly on the same footing in relationship to their neighbourhood. From a mathematical point of view, this equivalence of the lattice cells in an infinite crystal is expressed by what is usually called 'translational symmetry'. We have to investigate the nature of the normal modes of such a dynamical system.

Now a normal mode of a system represents a state of motion which can continue indefinitely (in the absence of perturbing forces) and independently of other possible modes. It corresponds to a single degree of

freedom of the system and it is therefore sufficient, when describing *any particular normal* mode, to specify the motion of any single atom in that mode. The displacements of all the other atoms *in the particular mode* are not independent quantities, but are uniquely expressible in terms of the displacement of that atom. A normal mode thus carries with it a description of the movement of any particular atom of the system, and the relative displacements of all the other atoms with respect to the particular atom chosen. In the most general case (lack of any symmetry) these relative displacements cannot be computed unless the nature of the forces in the system is known. The expressions for the displacements can only be derived from the equations of motion and involve the various *force constants.* The presence of symmetry in the system however permits us to write down some of these relative displacements at least in some of the normal modes. These relations are a consequence of symmetry only and hold good in any type of force field whatever, provided it leads to a quadratic form for the potential energy. A crystal represents a dynamical system with a high degree of symmetry, namely, the translational symmetry. The lattice as a whole may be displaced vectorially through three primitive lengths (or products or powers of these lengths), and still it returns to self-coincidence. Or, as has been stated earlier, all equivalent* atoms in the lattice stand on exactly the same footing in relationship to their neighbourhood. This equivalence has very important consequences and greatly reduces the complexity of the equations of motion and of the general quadratic form. In the fundamental paper which forms the introduction to this symposium, Sir C. V. Raman has formulated the equations of motion in terms of the most general force constants and has shown that this equivalence at once leads to the theorem that all equivalent atoms must have the same *amplitude* in every truly stationary normal mode. Further, the relative phases can either be the same or opposite with no other possibility. Starting with a particular atom (which for convenience we may locate at a lattice point) we can arrive at the nearest atom equivalent to it along a particular axis by moving through a primitive translation along that axis. According to Sir C. V. Raman, these two atoms have the same amplitude, but the same or opposite phases, in every normal mode. Once the relative displacement of these atoms is thus fixed, the translational symmetry at once fixes the displacement of every other atom equivalent to this along that axis. If the two nearest equivalent atoms have the same phase, the next one should also

* Two atoms are said to be equivalent when they can be brought over into one another by a translation operator, which should also bring the entire crystal into self-coincidence. With this definition the smallest unit cell contains no two equivalent atoms.

have the same phase, and so on. We would thus have a motion of which the phases may be pictured thus:

$$+ + + + + + \qquad (1)$$

On the other hand if they have opposite phases, the motion must be like

$$+ - + - + - + - \qquad (2)$$

These two results are a consequence of the fact that a primitive translation, being a symmetry element of the lattice does not alter the physical nature of a normal mode. The two possibilities given above arise for translations along one of the primitive axes. The other two axes have two such cases associated with each and the total number of distinct possibilities is thus $2^3 = 8$. In Sir C. V. Raman's notation, these cases are represented by

$$\alpha = \pm 1; \ \beta = \pm 1; \ \gamma = \pm 1 \qquad (3)$$

Here α, β, γ are the ratios between the displacement of any atom and its nearest equivalent atoms for primitive translations parallel to the axes. If $u_0 (= x_0, y_0, z_0)$ is the displacement any such atom chosen as the basis and u_1, u_2, u_3, those of the three atoms equivalent to it as above, we have,

$$u_0 = \pm u_1 = \pm u_2 = \pm u_3 \quad [u = x, y, \text{or } z]. \qquad (4)$$

The effective number of independent dynamical variables in the system is thus reduced to the number of degrees of freedom of the set of non-equivalent atoms in the crystal. This is $3p$ if p is the number of non-equivalent atoms in the crystal, and considering the 8 alternative possibilities which go with this set, we may speak of $24p$ dynamical variables which obey the relations (4). The next step is to write down the equations of motion and get the determinantal equation of order $24p$. Either a group theoretical analysis (to be given below), or a simple consideration of the symmetry shows that the eight possibilities are independent, mutually non-combining, and exclusive. Hence these relations can be substituted in the equations of motion one after another, and we get eight different determinantal equations of reduced orders $3p$ each. In the absence of further symmetry, no further reduction is possible and we get $(24p - 3)$ distinct frequencies (excluding 3 for pure translations). All these are different and symmetry is only helpful in separating them into the eight non-combining groups mentioned above. The $3p$ frequencies in each of these groups are coupled, *i.e.*, not separable by symmetry alone. The exact force field must be known to write down the normal co-ordinates and the frequencies for each separately. The presence of further symmetry in the crystal (rotations, reflexions, etc.) simplifies the matters much further and to cover these cases, group theoretical analysis is most helpful, from the point of view of rigour as well as simplicity. These questions will now be discussed.

2. *The Symmetry Group*

As emphasized earlier, every truly infinite lattice has translational symmetry represented by the three primitive translations, as well as their various products and powers. All these taken together form an Abelian group. In the dynamical problem at hand involving $24p$ dynamical variables only, the translation group assumes a very special character. It will be noticed from relations (1) and (2) that a basis atom has the same amplitude and the same phase as an equivalent atom derivable from it by translations $2\tau_x$, $2\tau_y$, $2\tau_z$ or products and powers of these lengths. The dynamic pattern is thus exactly repetitive in the lattice with a second-order super-cell as the repeating unit. In the investigation of these normal modes, therefore, $2\tau_x$, $2\tau_y$ and $2\tau_z$ are equivalent to identity. If $u_r = (x_r, y_r, z_r)$ is an atom in this super-cell, a translation $2\tau_x$, (or, $2\tau_y$, or $2\tau_z$) carries it into another atom $u_s\,(= x_s, y_s, z_s)$ which however is identical with u_r in displacement

$$u_r = u_s \tag{5}$$

Hence the effect of the translation $r \to s$ upon the dynamical variables* is the same as identity and all such translations, their powers and products, can be treated as identity. The translation group thus reduces to the Abelian group defined by

$$\tau_x^2 = \tau_y^2 = \tau_z^2 = \mathrm{E};\ \tau_x \tau_y = \tau_y \tau_x, \text{ etc.} \tag{6}$$

It has eight operations in all, namely, E, τ_x, τ_y, τ_z, $\tau_x \tau_y$, $\tau_y \tau_z$, $\tau_z \tau_x$ and $\tau_x \tau_y \tau_z$. It will be noted $\tau_x^{-1} = \tau_x$, etc. Any quadratic form for the potential energy which we may formulate must satisfy the symmetry of this group and it follows that the normal modes must come under one or the other of the irreducible representations of this translation group (excluding the case of higher symmetry for a moment). The group being Abelian and of order 8, we must have eight irreducible representations. These are derived easily from the generating relations (6).

$$x(\tau_x) = \pm 1, \quad x(\tau_y) = \pm 1, \quad x(\tau_z) = \pm 1 \tag{7}$$

leading to eight representations.† It is at once evident that (7) expresses the same thing as (3) or (4). Since we know that the normal modes coming under the different irreducible representations of a group are mutually

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* It must be remembered that the symmetry operations have significance for us only with respect to their effect upon the dynamical variables.

† See the work of Bhagavantam and Venkatarayudu in this connection (*Proc. Ind. Acad. Sci.*, 1941, **13**, 543 : 1939, **9**, 224). They have outlined fully the essential technique of group-theoretical analysis for crystals although their investigation is confined to the special case of equality of phase and amplitude for all equivalent atoms, *i.e.*, $x(\tau_x) = x(\tau_y) = x(\tau_z) = 1$.

independent and non-combining, it follows that the 8 alternative relations in (4) are independent and can be investigated each by itself. By substituting those relations in the equations of motion, we get, as explained earlier, 8 determinantal equations of order $3p$ each, giving the frquencies. That the $24p$ dynamical variables thus fall into 8 sets with $3p$ in each and that no further reduction is possible is easily verified by applying the standard methods of character tables and reduced characters. Taking the dynamical variables, we notice that each of these is sent into some other variable by the operations of the translation group except the identity which returns every variable to itself. Hence the reduced character of these operations on the dynamical variables is

$$\psi(\mathrm{E}) = 24p, \quad \psi(\mathrm{T}) = 0. \tag{8}$$

T stands for any one of the seven translation operations.

Hence the number of normal modes coming under any one of the representations of the translation group is given by

	E	τ_x	τ_y	τ_z	$\tau_x\tau_y$	$\tau_y\tau_z$	$\tau_z\tau_x$	$\tau_x\tau_y\tau_z$	n_i
A ..	1	1	1	1	1	1	1	1	3
B ..	1	−1	1	1	−1	1	−1	−1	,,
C ..	1	1	−1	1	−1	−1	1	−1	,,
D ..	1	1	1	−1	1	−1	−1	−1	,,
B′ ..	1	+1	−1	−1	−1	1	−1	+1	,,
C′ ..	1	−1	1	−1	−1	−1	1	1	,,
D′ ..	1	−1	−1	1	1	−1	−1	1	,,
A′ ..	1	−1	−1	−1	1	1	1	−1	,,
ψ_j (R)	24	0	0	0	0	0	0	0	

the formula $n_i = \frac{1}{N} \Sigma x_i^j(\mathrm{R})\, \psi_j(\mathrm{R})$ with the usual notation. It is evident from the table that the $3p$ frequencies in each group cannot be further separated from symmetry considerations alone. With suitably chosen force constants, all the normal modes can be separated and the frequencies calculated.

3. *Rotational and Reflexional Symmetry*

When a crystal lattice has extra symmetry by way of rotations and reflexions, several interesting features present themselves. In the first place, all the eight sets need not give rise to distinct frequencies. The $3p$ frequencies

in one set can become identical with the frequencies in one or more other sets and we may thus speak of "equivalent" sets. It is sufficient to calculate the frequencies for one such set among a group of equivalent sets, and the labour is thus greatly reduced. The normal co-ordinates corresponding to each other in two equivalent sets can always be brought over into one another by the application of a symmetry operation from the rotational and reflexional symmetry. Hence all the normal modes in the various equivalent sets can also be written from a knowledge of the nature of the modes in one set and the appropriate symmetry operations. A second type of simplification can arise from the fact that if a set of $3p$ frequencies has some other sets equivalent to it, there always exist the possibility of further reduction of the original set from symmetry considerations alone. The determinantal equation of order $3p$ can be further broken up into smaller determinants, using only considerations of symmetry. If the $3p$ modes give rise to s frequencies with varying weightages l, m, n, etc., we get at a very great simplification. Taking a frequency of this set which has a degeneracy of l, we need consider only one of the modes out of the l possible modes. The rest of the l modes give the same frequency and may be omitted from further consideration. Further, it has been explained above that every frequency from this set occurs in all the other sets equivalent to it. If we have r such equivalent sets, this particular frequency has a total number $l \cdot r$ normal modes associated with it, and a consideration of only one mode out of this number is enough to give the frequency. We begin the solution of the dynamical problem, therefore, by taking any one of eight cases given above, and writing down the number of equivalent sets it has. (The method for this is explained in the next paragraph.) If there is a total number r of such equivalent sets, we take only one out of it. Such a set has $3p$ normal modes associated with it, and every frequency from this set is repeated in the $(r-1)$ other equivalent sets and therefore has a minimum degeneracy of r. A further multiplication of degeneracy can arise if the frequency under consideration is the same for more than one out of the $3p$ modes. This type of degeneracy can be determined, and a complete analysis of the $3p$ modes can be made if the symmetry characters appropriate to the particular set under consideration are known. Once an analysis has been made for one such set, it is unnecessary to consider the other equivalent sets, (except to note the total degeneracy) and we may next proceed to consider another set out of the eight which does not occur in the first group of equivalent sets already studied. The number of sets equivalent to it are next noted and the process repeated as above until all the eight cases are fully covered.

The terms "equivalent sets" and "symmetry group appropriate to a set" can be more fully explained now. It will be noticed that each of the eight equivalent sets is defined by the corresponding characteristic values of the three primitive translations, *i.e.*, $\alpha = x(\tau_x)$; $\beta = x(\tau_y)$; $\gamma = x(\tau_z)$. Each case can be specified by giving the values of a *vector* whose components may be regarded as $x(\tau_x)$, $x(\tau_y)$ and $x(\tau_z)$. The eight vectors are thus given by (1, 1, 1); (−1, −1, −1); (1, −1, −1); (−1, 1, −1); −1, − 1, 1) and (1, 1, −1); (1, −1, 1); (−1, 1, 1). These correspond, as explained earlier, to the eight irreducible representations of the translation group. In the absence of further symmetry, the frequencies in each set are distinct. Let us now introduce some further symmetry, such as for example a plane of reflexion through the Z-axis bisecting the angle between X and Y axes. This operation keeps the Z-co-ordinate unchanged but changes X to Y and *vice versa*. Since every normal mode represents a state of vibration, it is capable of geometric picturization. If we have two normal modes of vibration, one involving movements of all the atoms along the X-axis and the second a similar movement along the Y-axis, these two modes have the same frequency for a system which has the plane of reflexion mentioned above. The vibration patterns can be carried over into one another by an operation from the symmetry group. This is the essence of degeneracy and in such a case we speak of equivalent modes. Since the eight vectors given above completely specify the nature of the modes for a group of $3p$ frequencies each, it is sufficient to apply the symmetry operations directly to them. The vectors can be given a geometric representation and the set of all vectors carried over into one another by the symmetry operations form an "*equivalent set*". Under the operation σ_v, $z \rightarrow z$, $x \rightleftharpoons y$, the vectors (1, 1, 1); (−1, −1, −1); (−1, −1, 1); and (1, 1, −1) are unchanged or "*left invariant*" while (1, −1, −1) and (−1, 1, −1) are carried over into one another with similar effect on the remaining two vectors (1, −1, 1) and (−1, 1, 1). Hence in a system with symmetry σ_v, the eight vectors fall into six distinct sets, and there is a minimum degeneracy of two for every frequency of the last two sets. If the system has got similar reflexion about the X and Y axes also, we get the following system of non-equivalent sets.

(i) (1, 1, 1)
(ii) (−1, −1, −1)
(iii) (1, −1, −1), (−1, 1, −1); (−1, −1, 1)
(iv) (−1, 1, 1); (1, −1, 1); (1, 1, −1) (10)

We thus need consider only (1, 1, 1); (−1, −1, −1) and one vector each form (iii) and (iv) thus making four in all. Frequencies associated with any

one vector from (iii) are repeated in the other two vectors and so we have a minimum degeneracy of three. If the normal modes associated with $(1, -1, -1)$ say are known, those in $(-1, 1, -1)$ and $(-1, -1, 1)$ are derivable from these by simple application of the reflexion operators through Z and Y axes. A similar statement holds for the modes in (iv).

The easiest method of determining equivalent sets is to directly picture the translation vectors τ_x, τ_y, τ_z instead of their characteristic values. These vectors can be thought of as lying along the three axes and the effect of the symmetry operations upon these is at once evident. Thus σ_y along the Z axis has the following effect on τ_x, τ_y, τ_z.

$$\tau_z \rightarrow \tau_z, \quad \tau_x \rightleftharpoons \tau_y.$$

Hence $x(\tau_z) \rightarrow x(\tau_z)$; $x(\tau_x) \rightleftharpoons x(\tau_y)$.

Applying this operation on the eight representations given in (9), we get straightaway at the distribution given above. The representations A, A′, D, D′ are left invariant, while B and C are carried over into one another with corresponding results for B′ and C′. B and C and similarly B′ and C′ become "equivalent", under the operation σ_y. We may thus speak of "equivalent" representations instead of equivalent vectors and this language is more suitable to the group theoretical presentation to be given below. If the system has three planes of reflexion about the X, Y and Z axes, the representations B′, C′ and D′ become equivalent and similarly B, C, D also. It must be understood that these representations are not equivalent in the translation group, but become so in the extended group which includes the reflexions. In fact, if the character table for this extended group is written down, it will be noticed that B, C, D combine there in giving rise to a single representation of degree 3. This is a standard method of deriving the character tables and may be employed if we choose to derive the degeneracies and the normal modes straight from the character table for the full group. Actually this introduces unnecessary complications, since all that has been explained before really has the aim of *analyzing* a normal vibration of degree 3 into its constituent vibrations each of degree 1. The process of *compounding* them back again has no importance except to satisfy ourselves that they do really form an equivalent set of representations. Further, the work of Seitz (next section), shows that the modes associated with B can be considered quite independently of the other two equivalent representations C and D. Equivalence brings in the simplification that C and D need not be considered again, while it preserves the original independence of the three representations B, C, D. An investigation of the modes associated with A, A′, B and B′ is thus quite sufficient to evaluate the frequencies. We will now show how this can be done.

Here we have to explain the significance of the terms " invariance of a vector " (or representation) and the " group of a vector " used in the previous paragraphs. In the example of a group of three planes of symmetry given above, it will be noticed that some of the vectors or representations are changed into themselves by some or all of the symmetry operations. Thus the representations $x(\tau_x) = x(\tau_y) = x(\tau_z) = \pm 1$ are changed into themselves by the three reflexions, while from the very definition, the translations leave every representation of their group invariant. The totality of symmetry operations which leave a vector unchanged is known as *the group of the vector* under consideration. In this case it is the total symmetry group G composed of all the translations and the reflexions. The representation $x(\tau_x) = 1$, $x(\tau_y) = x(\tau_z) = -1$ is however left invariant only by the reflexion plane through the X-axis while the other two reflexions carry it over into the other two equivalent representations. Hence the group of the vector in this case consists of the translations, the reflexion plane σ_x and the other operations derivable by the association of the translations with σ_x. There exist two other similar groups for the other two vectors, derivable by fixing σ_y and σ_z, with the translation group. The structure of the *group* of a vector is of fundamental importance when analyzing the nature of the $3p$ normal modes associated with that vector. It has been shown by Seitz that all representations associated with a vector must come under one or the other of the irreducible representations of the group of that vector. This means that all the $3p$ normal modes going with one vector out of the eight must have the symmetry requirements of one or the other of the irreducible representations of the *group of that vector*. Hence if the structure of this group is known, the normal modes going with this vector are determined by the usual and standard methods. Let the group of this vector be G_1 consisting of operations P, Q, R, etc. We take the $24p$ dynamical variables of the unit cell and study the effect of each of the operations P, Q, R, etc., on these variables. The reduced character $\psi(R)$ of each operation R of this group is thus calculated. From the character table for G_1, the number of modes coming under any irreducible representation of G_1 is given by the standard formula

$$n_i = \frac{1}{N_1} \Sigma \psi(R)\, x^i(R). \tag{11}$$

Here N_1 is the order of G_1 and the summation runs over all elements of G_1.

It will be noticed that G_1 is actually a space group containing translations and as such its character table is not among the standard and well-known tables. A derivation of the table might be attempted, but it is quite

unnecessary for our prosent work. An alternative elegant method is given in the next section and by its use, the formula is also simplified very greatly. To proceed further however, we need to explain the exact mathematical analysis conducted by Seitz,[1] Clifford,[2] etc., upon which all the statements made above rest for their validity.

4. *Group Theoretical Analysis**

An illuminating treatment of the full mathematical technique needed for the reduction of space groups has been given by Seitz[1] and we note down here only the results of his investigation. For the other points the reader is referred to his original paper. It will be remembered that normal vibrations actually belong to the irreducible representations of the symmetry group of a system. Here we have a space-group composed of rotations, reflexions and translations. So the object is to reduce this group into its irreducible representations, Seitz has actually shown that these representations can be gradually built up starting from the irreducible representations of a translation group. (The translation group is an invariant subgroup of the space-group.) In our present problem these are only eight in number as given in Table 9. The effect of rotational and reflexional symmetry elements upon these representations is such that a particular representation is either completely left invariant (in the sense fully explained already) or totally carried over into another representation which, for this reason, is equivalent to it. This follows, as shown by Seitz, from the Abelian and invariative nature of the translation subgroup. Hence if $\Sigma_1, \Sigma_2, \ldots \Sigma_r$ are such a set of equivalent representations, the effect of the symmetry group on these is to ensure that $\Sigma_r \rightarrow \Sigma_r$ or $\Sigma_r \rightarrow \Sigma_s$ with no linear combination being possible between Σ_r and Σ_s.† From this it follows that the representations of the translation group can be regarded as mutually independent and consideration can be confined to any single representation out of an equivalent set, quite independently of others. The next step is to determine the symmetry characteristics associated with each such representation of the translation group. These are determined by the *group* which leaves the *vector invariant* and its irreducible representations. Seitz has shown that every representation associated with a vector must come under one or the other of the irreducible representations of the group of that vector. As observed earlier, this group is a space-group and sometimes may include the totality of all

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* The reader more interested in practical applications of the theory may omit this section and proceed straightaway to the next one where a summary of the whole method is given.

† The emphasis is that we can choose at least one frame of reference in which the representations are of the type indicated above.

the symmetry operations in the crystal lattice, *e.g.*, the (1, 1, 1) vector. The essential point is to build up the representations of a larger group from those of a self-conjugate sub-group in an ascending order, starting from identity and in such a manner that we pass through a series of subgroups of the group of the vector. These subgroups should form a composition series, and in such a series the representations of any group G_r can be derived from the immediate next group G_{r-1}. Every representation G_{r-1} is taken and the effect of the elements of G_r upon it is studied. G_r is actually derivable from G_{r-1} by appending a cyclic group to it. The factor group $\frac{G_r}{G_{r-1}}$ is cyclic and consists of elements, say, E, S, $S^2, \cdots S_{n-1}$. A particular representation Σ say of degree m of G_{r-1} is chosen and the effect of S upon it is studied. If this representation is left invariant by S, it is left invariant by all the others S^2, S^3, S_{n-1} and the result will be (n) distinct representations in G_r, each of degree m. All these representations have the same characteristics so far as the elements of G_{r-1} are concerned, but differ from one another in the characteristic values of S, S^2, etc. On the other hand, if S carries Σ into Σ', the others also do so and we get a set of representations $\Sigma, \Sigma', \Sigma''$ of G_{r-1} which become equivalent in the extended group. All these join together to form an irreducible representation of higher degree in G_r.

So far as our work is concerned, the above mathematical detail is unnecessary except in special cases like the diamond lattice. The only essential point is to notice that these representations are built up starting from the representations of a self-conjugate subgroup which is the translation group in our case. When we are considering the group of a vector, it is enough if we build up only such representations of the translations group as belong to this particular vector. For example, it was observed already that the group of the vector (1, 1, 1) (*i.e.*) $x(\tau_x) = x(\tau_y) = x(\tau_z) = 1$, is the entire space group since it is left invariant by every operation. However, in considering modes associated with this vector, we are not interested in every possible representation of this space group. In the process of building up, we confine our attention only to the representation (1, 1, 1) of the translation group. Only such representations of the space group which are derivable from $x(\tau_x) = x(\tau_y) = x(\tau_z) = 1$ by the process of building up as explained above, need be considered. In other words, we have to deal with, firstly, a representation vector of the translation group and secondly, all representation of the group of that vector which are derivable from the original representation of the translation group. These two representations correspond with one another in the two groups and Clifford[2] calls this correspondence as the representations induced in an invariant subgoup. He

has proved a very elegant theorem showing that all representations in G_1 associated with a definite representation Σ of a self-conjugate subgroup T can be uniquely decomposed as the direct product of two representations, one being Σ itself and the other being an irreducible representation of the factor group G_1/T. The condition is that G_1 should be capable of being written as the product of two groups, one the translation group itself and the other a *point group* of elements. The symmetry of the diamond lattice does not satisfy this condition and exceptional cases like these will be dealt with in a separate paper. In general, this condition is satisfied and Clifford's results show that the representations of G_1 which are associated with a particular representation of the translation group are merely the direct product of that particular representation and an m-fold representation of the point group elements in G_1. The character tables for all standard crystallographic point groups are known and thus the problem is easily solved. The complexity of the problem is greatly reduced if we choose as dynamical variables the $3p$ displacements only of the atoms in the smallest unit cell. The other $21p$ displacements of the atoms in the neighbouring cells are to be regarded as dependent upon these and expressible in terms of these variable by relations of the type (4). These relations differ from vector to vector, and covering all the 8 cases, we get the total number of degrees of freedom. Considering $3p$ variables only in the unit cell and a specified vector, the reduced character ψ upon these variables can be calculated. Thus if the vector is $x(\tau_x) = x(\tau_y) = x(\tau_z) = 1$, the effect of each of the translations upon the $3p$ variables in the unit cell (when the state of vibration belongs to the above vector) is to send each variable into another which is the same with repsect to it in amplitude and phase. Hence all the variables in the unit cell may be regarded as unchanged by the translation operators in this particular vector.

$$\psi(\mathrm{R}) = 3p = \psi(\mathrm{E})$$

for every R of the translation group. The effect of the other operations can likewise be studied. If the vector is $x(\tau_x) = -x(\tau_y) = -x(\tau_z) = 1$, τ_x keeps the set of $3p$ variables uncharged while τ_y and τ_z change each of them to its oppisite phase.

Thus
$$\begin{aligned} \psi(\tau_x) &= 3p = \psi(\mathrm{E}) \\ \psi(\tau_y) &= -3p = \psi(\mathrm{E})\, x(\tau_y) \\ \psi(\tau_z) &= -3p = \psi(\mathrm{E})\, x(\tau_z) \end{aligned} \qquad (12)$$

similarly $\psi(\tau_z \tau_y) = +3p$, etc.

From these examples, and simple considerations, it is clear that $\psi(\mathrm{T}_n) = \psi(\mathrm{E})\, x(\mathrm{T}_n)$, T_n being an element of the translation group and $x(\mathrm{T}_n)$ its

character associated with the vector under consideration. Further, it is obvious that

$$\psi(\mathrm{RT}_n) = \psi(\mathrm{R})\ x(\mathrm{T}_n) \tag{13}$$

The results of Clifford show that

$$\begin{aligned} x^i(\mathrm{T}_n) &= x^i(\mathrm{E})\, x(\mathrm{T}_n) \\ x^i(\mathrm{RT}_n) &= x^i(\mathrm{R})\, x(\mathrm{T}_n) \end{aligned} \tag{14}$$

where R is any element of the point-group symmetry. $x^i(\mathrm{T}_n)$ is the characteristic of T_n in the ith representation of the group G_1 which is the group of a specific vector. $x(\mathrm{T}_n)$ is the character of T_n for that vector.

Relations (13) and (14) very greatly simplify the formula (11). We have

$$n_i = \frac{1}{\mathrm{N}_1} \Sigma\, \psi(\mathrm{R})\, x^i(\mathrm{R}) \tag{15}$$

the summation running over all the group elements, *i.e.*, the rotations and reflexions as well as their products with the translations. The summation over the latter can however be entirely dispensed with, by the use of relations (13) and (14). We have,

$$\psi(\mathrm{RT}_n)\, x^i(\mathrm{RT}_n) = \psi(\mathrm{R})\, x(\mathrm{T}_n)\, x^i(\mathrm{R})\, x(\mathrm{T}_n) = \psi(\mathrm{R})\, x^i(\mathrm{R}) \tag{16}$$

since $x(\mathrm{T}_n)\, x(\mathrm{T}_n) = 1$ always.

This shows that the product $\psi(\mathrm{R})\, x^i(\mathrm{R})$ is the same for a parent rotational or reflexional element R as well as its derived operations RT_n for all T_n. Hence the summation over the latter is merely to multiply each term by the number of translation operators. Since the order of the translation group divides the order of the group G_1 the result being the order of the point group element in G_1, we can express the result as

$$n_i = \frac{1}{m} \Sigma\, \psi(\mathrm{R}) x^i(\mathrm{R}) \tag{17}$$

Here the summation runs over the point group elements of G_1 only and m is their total number. Since Clifford[2] has shown that the representations of G_1 are the direct product of representations of the translation group with those of $\frac{\mathrm{G}_1}{\mathrm{T}}$, it follows that $x^i(\mathrm{R})$ belongs to the representations of the point group only. Hence it is no longer necessary to work out the character table for a space group and the information about the point group contained in the group of a vector is quite sufficient to evaluate the normal modes associated with that vector. We shall now briefly summarize all the important points discussed above.

5. *Brief Recapitulation*

To evaluate the normal modes of a crystal lattice on the basis of the Raman theory of lattice vibrations,[3] *choose any one of the irreducible representations of the translation group. Find out the symmetry operations, rotations and reflexions which leave this vector unchanged and write down the character table for this point group.** *Choose as dynamical variables the* 3p *independent displacements of the atoms in the smallest cell and write down the character* ψ *of each operation of this point group when acting on these* 3p *variables (during a state of vibration represented by the vector under consideration). Formula* (17) *then gives straightaway the number of normal modes coming under any one of the irreducible representations of this point group. Their symmetry characters are known from the character table and so the normal co-ordinates can be written down by the usual methods. If the character table for the point group involves representations of degrees* 2 *and* 3 *and if the normal modes are not evident at once, we repeat the above process again for this point group. What we have actually done in this work is to analyse the representations of a space group (which are usually of a high degree) into their constituent representations much more convenient to handle. This analysis arises from a choice of the self-conjugate subgroup of the translations. If the point group associated with a vector has representations of degrees* 2 *or* 3, *they can be analyzed exactly as above into smaller representations. Once the normal modes are known the frequencies are calculated by the usual methods.*†

The next step is to find out the number of representations of the translation group which are equivalent to the vector under consideration. These give the same set of frequencies and only the degeneracy is increased. They need not be considered separately. If these exist $(r-1)$ *vectors equivalent to a vector, every frequency associated with it has a minimum degeneracy of* r. *A frequency with* m*-fold degeneracy and associated with a vector for which* $(r-1)$ *other equivalent vectors exist has a total degeneracy of* $m \times r$. *Investigation of the rest of the vectors is conducted likewise until all the possibilities are exhausted.*

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* This method is not directly applicable for all the eight phase vectors of a diamond lattice. A simple modification is required which will be dealt with in a separate paper.

† See Bhagavantam and Venkatarayudu's work mentioned earlier.

Summary

A group theoretical method to deal with the harmonic vibrations of a general crystalline lattice is indicated in this paper. Sir C. V. Raman's theory of lattice vibrations[3] is the basis of the work and it is indicated how the normal modes, frequencies, their degeneracies, etc., can be rigorously derived. Applications of this work to specific problems are given in another paper in this symposium.

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RAMAN SPECTRA OF CRYSTALS AND THEIR INTERPRETATION

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1. Introduction

Its universal applicability, the simplicity of the technique, the precision of the results obtained and the ease of their interpretation make the Raman effect a powerful instrument for the study of the structure of matter. The information yielded by Raman spectra has been of great value in the investigation of relatively simple molecules as well as of the more complicated polyatomic ones. Its utility in the investigation of the physico-chemical problems set by the crystalline state of matter is equally great. An appreciation of this fact was no doubt responsible for the late Lord Rutherford having stated in his Presidential Address to the Royal Society in December 1930 that the Raman effect "has proved and will prove an instrument of great power in the study of the theory of solids". If this prophecy has not been fulfilled to the maximum extent, it is because the physics of the solid state has been dominated for many years by theories which had their birth before the discovery of the effect, and which, it is safe to say, would probably not have been put forward or received general acceptance if the experimental information furnished by Raman spectra regarding crystals had been available at the time. The reference here is to the well-known theories of solid behaviour originally put forward about the same time (1912) by Debye and by Max Born and which have a common central core in their structure of thought.

It is a significant fact that, subject to some noteworthy qualifications and exceptions, the modes of atomic vibration appearing in the Raman spectra of crystals are represented by sharp lines irrespective of the nature of the substance or of the nature or frequency of the vibrations. In his Faraday Society address of September 1929, Sir C. V. Raman pointedly drew attention to this feature and suggested that the monochromatism of the atomic vibrations is a characteristic consequence of the regular ordering of the ultimate particles in the crystalline state of matter. More recently (1941), he has returned to this subject and put forward a new theory of the specific heat

of crystals in which the basic notions of the Debye and Born treatments are rejected as untenable. In the introductory paper (Raman, 1943) of the present symposium, this new theory has been given a precise mathematical form, and it is shown that every crystal has $(24p - 3)$ fundamental modes of atomic vibration with monochromatic frequencies. Of this number, $(3p - 3)$ modes may be described as oscillations of the p interpenetrating atomic lattices of which the crystal is composed, while the remaining $21p$ modes are oscillations with respect to each other of various important planes of atoms in the crystal. The number of distinct frequencies is considerably reduced when the crystal has a high degree of symmetry. Both the number of frequencies and the geometry of the modes can be fully worked out from symmetry considerations in the case of simple structures. For instance, diamond has eight fundamental frequencies, rock-salt has nine, fluorspar has fourteen, and so forth.

The Raman dynamics of crystal lattices has now reached a form in which it can be worked out and developed in various directions. It is important, however, to show that the ideas on which it is based are well founded, and that on the other hand, the alternative theories which now hold the field are irreconcilable with the experimental facts. It is here that the evidence of the spectroscope is of the highest importance. In another paper appearing in the present symposium, Mr. Pant (1943) has reviewed the extensive and entirely independent evidence available from the published studies on the luminescence and absorption spectra of crystals at very low temperatures. In the present paper, the Raman effect evidence will be marshalled and discussed in its relation to the theories of crystal dynamics.

The numerous papers which have appeared on the Raman spectra of crystals may be placed broadly in two divisions, namely those in which the emphasis is respectively on the chemical and on the physical aspects of the subject. Many more investigations belong to the former group than to the latter, but they have nevertheless yielded data of great significance to crystal physics. The researches on the Raman effect designed expressly to elucidate the fundamental aspects of crystal physics are not very numerous. As we shall see, however, the results they have furnished are quite sufficient to yield a decisive answer to the theoretical issues now under consideration.

2. *The Case of Rock-Salt*

The Debye theory assumes from the start that the atomic vibrations are of the same general nature as the elastic vibrations of the solid. The Born theory rests on a fundamentally similar assumption, which appears as the so-called " postulate of the cyclic lattice ". It is scarcely necessary to discuss

here the Debye theory in detail, as it has no explanation whatever to offer for the appearance of discrete lines in the Raman spectra of crystals. According to Born, the vibration spectrum of the crystal may be divided into branches which he classifies respectively as the "optical branches" and the "acoustic branches", all these, however, being essentially continuous spectra. The experimental fact that the Raman spectra exhibit sharply defined frequencies stands in obvious contradiction with these assumptions. To escape this fundamental difficulty, an ingenious argument has been put forward which we shall examine in detail later in this paper. Before doing so, we shall proceed to consider the actual experimental facts in the case of the rock-salt lattice, which is a particularly suitable substance in view of the fact that much of the work of Born and his collaborators has centred round this substance and its analogues, the alkali halides.

We owe to Rasetti (1929, 1930) the development of a remarkably useful technique for the study of the Raman effect, the value of which has been demonstrated by the resounding success with which he himself applied it in several cases of fundamental interest. In this field of research generally, and especially in investigating substances such as gases or vapours which scatter light only feebly, or crystals which exhibit only feeble Raman spectra, it is essential to employ a light source which emits the most intense possible and highly monochromatic radiation, and that there should be no unwanted radiations and especially no continuous spectrum accompanying the same. Further, it is highly desirable that the exciting radiation (but not the excited ones) should be removed from the light scattered by the medium before its entry into the spectrograph, as otherwise the photographic plates would be fogged by its general diffusion within the instrument. Rasetti secured all these advantages and in addition the enormously increased scattering power of short wave-length radiations arising from the λ^{-4} law, besides enabling the high resolving power which even small quartz spectrographs possess in the ultra-violet region to be utilized, by employing the 2537 A.U. monochromatic radiations of mercury vapour under special conditions which ensured that *only* this radiation and *none* other would give an observable Raman effect. The technique consists in using a low-pressure quartz mercury arc in which the mercury vapour is prevented from reaching any considerable density, and from absorbing the 2537 radiation emitted by itself. This is accomplished firstly by very effective water-cooling, and secondly by squeezing the discharge against the walls of the quartz tube by the field of a specially designed electromagnet. A filter of mercury vapour at room temperature is placed in the path of the scattered light emerging from the substance under study to absorb the 2537 radiation. This filter works so effectively that

some of the feeble mercury lines which have intensities negligibly small in comparison with the 2537 radiations and which therefore give no observable Raman effect nevertheless appear stronger than the 2537 line in the recorded spectra. This is in particular noticeable with regard to the neighbouring 2535 A.U. line which appears adjacent to the 2537 line in the recorded spectra. In no case, however, does it give any detectable Raman shifts, indeed not even those excited most intensely by the 2537 excitation.

Rasetti investigated many crystals using his technique and with notable success. His greatest achievement in this field was the successful recording of the Raman spectrum of rock-salt which previous investigators had reported as giving no observable effect. The feebleness of the phenomenon can be judged from the fact that with a large prism of rock-salt 5 centimetres thick, an exposure of 8 hours reinforced by internal reflections within the prism had to be given, while a few minutes under the same conditions sufficed for recording the spectrum of quartz. In his preliminary report in *Nature* (1931), Rasetti remarked on the "very peculiar structure" of the Raman spectrum of rock-salt. A rather poor reproduction of the spectrogram appears with his paper in the *Nuovo Cimento* (1932). There is a better reproduction accompanied by a microphotometer record in the joint paper by Rasetti and Fermi (1931) in the *Zeitschrift fur Physik*. But the most satisfactory reproduction is that appearing on page 139 of the German translation of Fermi's book *Moleküle und Krystalle* (1938). In this reproduction, the discrete character of the spectrum is quite evident, and the positions of the intensity maxima can be read off from it directly with a glass scale. The details of the structure as thus seen and measured are confirmed by their complete correspondence with the peaks or kinks seen in the microphotometer record appearing immediately above the reproduced spectrogram. A further striking confirmation is furnished by the fact that the pattern is also visible in the reproduction as an "antistokes" Raman spectrum in the extremely clear region lying on the short wave-length side of the 2537 exciting radiation. The details of this region also appear quite distinctly in the microphotometer record.

One notices that the spectrum consists of nine discrete and clearly resolved Raman lines. Their frequency shifts from the exciting 2537 radiation and their approximate widths are recorded in Table I. This shows both the "Stokes" and "antistokes" Raman shifts as determined from the spectrograms and microphotometer records. From the latter records, rough computations have been made of the relative intensities of both the Stokes and antistokes Raman lines. These results are also included in the table. The observed value of the ratio of the intensities of the Stokes

to the antistokes Raman lines is in reasonable agreement with that to be expected from Placzek's well-known formula, as will be seen from the comparison made in the table.

TABLE I

Raman Spectrum of Rock-Salt

Serial Number	Frequency shifts of the Stokes line in cm.$^{-1}$	Approximate breadth in cm.$^{-1}$	Relative intensity taking the intensity of 235 Stokes line as 10	Frequency shift of the anti-stokes line in cm.$^{-1}$	Approximate breadth in cm.$^{-1}$
1	134	diffuse	3·3	150?	
2	183	25	5·8	189	
3	235	5	10	239	6
4	256	13	8·9	265	
5	281	15	9·9	278	15
6	294	14	10·3	288	15
7	317	14	10	311	15
8	340	8	8·9	339	10
9	350	8	9·2	349	10

Serial Number	Relative intensity taking the intensity of 235 Stokes line as 10	Observed intensity ratio of the Stokes to antistokes line	Calculated intensity ratio using Placzek's formula	Fundamental frequency in cm.$^{-1}$
1	2·4	1·4	1·9	67
2	2·9	2·0	2·3	91
3	3·2	3·1	3·0	117
4	2·4	3·7	3·3	128
5	2·7	3·7	3·7	140
6	2·8	3·7	3·9	147
7	2·6	3·9	4·3	158
8	2	4·5	4·8	170
9	2	4·6	5·0	175

As will be seen from the figures in the third column of the table, some of the observed lines are quite sharp while others are only moderately so. The line having a frequency shift of 235 cm.$^{-1}$ exhibits exceptional sharpness and intensity both on the Stokes and antistokes sides, and being situated in a clear region and well separated from the remaining lines is a conspicuous feature in the spectrogram. The agreement of the frequency shifts as measured from the Stokes and the antistokes regions, as also of their approximate widths on the two sides, and the fair agreement of the observed intensity ratio of the Stokes to the antistokes lines with that calculated from Placzek's formula leave no room for doubt that the figures shown in the second column are a correct description of the Raman spectrum of rock-salt.

We shall now proceed to examine the facts stated above in the light of the existing theories. As is well-known, the crystal structure of rock-salt is made up of two interpenetrating face-centred cubic lattices. The unit cell is a rhombohedron with one sodium ion and one chlorine ion contained in it. According to Born's theory, a crystal with p non-equivalent atoms in the unit cell would in general have $(3p-3)$ "limiting frequencies" in the optical branch, the remaining 3 degrees of freedom going to the acoustic branch of the vibration spectrum. The former number may, however, be reduced by the symmetry properties of the crystal to a smaller figure. In the present case $p = 2$, and the crystal belongs to the highest class of cubic symmetry. The 3 possible "limiting frequencies" of the optical branch are therefore reduced by degeneracy to one. As the result of the manner in which the sodium and chlorine ions are grouped around each other, the oscillation of the two sets of ions with respect to each other which has this frequency, would be active in infra-red absorption and would correspond to the reststrahlen frequency of 52μ observed in rock-salt. For the same reason, this vibration should be inactive in the Raman effect. This explains the inability of some of the earlier workers, notably Schæfer (1929) to record any Raman line with rock-salt, and indeed also in the other alkali halides.

Accepting the view-point of the Born dynamics, Fermi attempted to give a theoretical explanation of the observed Raman spectrum of rock-salt in the joint paper by himself and Rasetti (1931) and succeeded to the extent of showing why the high-frequency limit of the Raman spectrum agrees with twice the known reststrahlen frequency of rock-salt. He frankly, however, admitted his inability to explain the other features observed in the spectrum in the following words (translated from the original German):—"In order to calculate the intensity distribution in the Raman spectrum, special assumptions are necessary regarding the influence of the polarisability of the crystal atoms by the elastic displacements. It appears therefore impossible for the present to explain the fine structure of the observed spectrum."

The appearance of nine discrete frequencies in the Raman spectrum of rock-salt, on the other hand, finds a natural and ready explanation in the new theory of the dynamics of crystal lattices put forward by Sir C. V. Raman in the introductory paper in this symposium. In a paper appearing elsewhere in this symposium, Chelam (1943) has worked out the complete vibration spectrum of rock-salt basing himself on the Raman theory of crystal dynamics. The main results of his paper are summarised below. The number of non-equivalent atoms in the rock-salt lattice is 2. Hence the total number of degrees of freedom will be $2 \times 8 \times 3$ or 48, of which 45 will appear as the atomic frequencies and the remaining 3 go over into the

"elastic spectrum". The 45 frequencies would be reduced by degeneracy to 9 distinct ones as shown below:

	Degeneracy
(1) The sodium and chlorine lattices vibrating against each other	4
(2) The alternate planes of sodium atoms parallel to the octahedral faces oscillating against each other, normal to themselves	4
(3) The alternate planes of the chlorine atoms parallel to the octahedral faces oscillating against each other, normal to themselves	4
(4) The alternate planes of sodium atoms parallel to the octahedral faces oscillating against each other, parallel to themselves	8
(5) The alternate planes of chlorine atoms parallel to the octahedral planes oscillating against each other, parallel to themselves	8
(6) & (7) The coupled oscillations of the sodium and chlorine atoms in the planes parallel to the cube faces, normal to these faces	3 each.
(8) & (9) The coupled oscillations of the sodium and chlorine atoms in the planes parallel to the cube faces along these planes	6 each.

Because of the symmetry properties of the rock-salt structure, all these nine modes of vibration would be inactive in Raman effect. But it has been pointed out from theoretical considerations by Placzek (1934) and recently by Bhagavantam and Venkatarayudu (1939) that the first overtone of every normal vibration is active in the Raman effect, irrespective of whether the fundamental is permitted or forbidden. The observed nine frequencies in the Raman spectrum of rock-salt are therefore the overtones of the nine fundamental modes of vibration enumerated above. The values of these fundamental frequencies calculated from the observed Raman shifts are given in the last column in Table I.

3. The Structure and Sharpness of the Raman Lines

In the Raman dynamics of crystal lattices, the monochromatism of the $(24p - 3)$ modes of vibration possible appears as a natural consequence of the fundamental property of crystal structure that it is a three-dimensional repetition pattern in space of practically infinite extension. Any

circumstance that modifies or alters the periodic structure of the crystal must modify the monochromatism of the vibration frequencies to an extent depending on the particular circumstances of the case. An imperfection or mosaicity of the crystal structure and the disturbing influence of thermal agitation may be mentioned as such circumstances. The extent of their influence on the character of the spectra would depend on the individual case, including especially the nature and strength of the binding forces within the crystal, the geometric character of the particular mode of vibration and the masses of the vibrating atoms, ions or molecules. In agreement with these indications of the theory, we find that though Raman spectra of crystals usually consist of well-defined lines with accurately measurable frequency shifts, their sharpness varies from crystal to crystal and even in the same crystal, it may be different for the different lines. It may be and usually is also a function of temperature. Speaking broadly, it may be said that the lines with small frequency shifts are less sharp than the lines with high frequency shifts, but there are numerous exceptions to this rule. Further, there are many examples which suggest that vibrations controlled by valence forces appear as extremely sharp lines in the Raman spectrum, while vibrations controlled by ionic or molecular attractions, appear as rather broad and diffuse lines.

The explanations which have been offered for the appearance of sharp lines in the Raman spectra of crystals on the basis of the Born lattice dynamics may now be briefly stated and examined. They rest on the idea that only the "limiting frequencies" of the lattice, *viz.*, those having great phase-wavelengths could appear in the observed spectra. As a consequence of the postulate of the cyclic lattice, however, vibrations with smaller phase-wave-lengths are enormously more numerous than those with longer phase-wave-lengths, and they would give frequencies different from the latter, and thereby build up a continuous spectrum. What is actually observed in light-scattering, however, is something very different, and to remove this obvious contradiction between the theory and the experimental facts, it is suggested that the frequencies of the vibrations of shorter phase-wave-lengths disappear from the spectrum by reason of the optical interference of the effects due to them arising from different elementary volumes in the crystal. While this argument is no doubt ingenious, it is obvious that it assumes that the atomic vibrations in the lattice have perfectly ordered phase-relations over volume elements sufficiently large for such interference to give, on the one hand the frequencies actually observed with the sharpness and intensities found in experiment, and on the other hand to extinguish completely the frequencies assumed to exist but to be unobservable.

Perhaps the most appropriate comment which could be made is that while, as we have seen in the case of rock-salt, the Born theory does not on the one hand, explain the features actually observed in the spectra, it postulates on the other hand a whole spectrum of frequencies for which there is no observational evidence. Further, to remove the conflict between fact and theory, a hypothetical assumption is made for which there is no experimental justification. In fact, it may be said that the entire approach made in the theory is artificial in character. It should be added that neither ***a priori*** considerations or any actual facts of observation compel us to assume the existence of coherent phase-relationships of the lattice vibrations of high frequency over extended volumes of the crystal. The mosaicity of most actual crystals, the existence of thermal agitation and above all, the known facts about the thermal conductivity of solids indeed make it difficult to accept such an assumption without large reservations.

4. The Force-Fields in Crystals

In not a few cases, the experimental facts established by Raman effect studies with molecular systems, *e.g.*, gases and vapours at ordinary and at higher pressures, liquids, solutions, mixtures and fused melts, form a useful starting point for the interpretation of the phenomena observed with crystals. The greater density and consequently increased magnitude of the force-fields, as also the regular ordering of the units characteristic of the crystalline state have, of course, to be taken into account in this connection. It is obvious also that the classification of molecular movements into three classes as translations, rotations and vibrations, which is quite appropriate for gases and which is not quite so appropriate for liquids ceases to have a strict scientific significance in a crystal. All movements should be considered as atomic displacements and described as time-periodic variations from the standard atomic configurations prescribed by the crystal structure. Indeed no other way of describing the movements is open to us in the case of those crystals in which no specific molecular or ionic configurations can be recognized. With typically molecular or ionic lattices, however, it is convenient to speak of "internal vibrations", "rotational oscillations" and "translatory oscillations", and these descriptions may even roughly correspond to specifiable ranges of vibration frequency. In using these terms, however, it should be remembered that they cannot be an accurate description of the actual displacements in the crystal.

Subject to the limitations indicated, we may consider "ionic" and "molecular" crystals and discuss in turn each of the three classes of vibration. Raman effect studies with liquids, mixtures, solutions and melts show

that the internal vibrations are only influenced in a secondary degree by the state of aggregation. When the irregular arrangements existing in fluids is replaced by the regular ordering characteristic of a crystal, the force-fields surrounding individual ions or molecules become definite. *In consequence, we should expect the "internal frequencies" of the ions or molecules in crystals to become as precisely specifiable as in gases, but with definite changes due to the influence of the force-fields. Indeed, it should be possible to evaluate the changes in these frequencies as between the gaseous, fluid and crystalline states by considering the magnitudes of the force-fields, and vice-versa from the observed frequency changes to evaluate the force-fields.* This principle has been applied with success at this Institute and its utility thereby established.

Raman effect studies in fluid media show that the freedom of rotation of the ions or molecules is greatly hindered in fluids by the density of the aggregation and by the viscosity of the medium. In crystals the molecules or ions occupy specific orientations and the force-fields in which they lie should therefore be exactly definable. Hence the ions or molecules in crystals should have precisely definable frequencies of rotational oscillation about their positions of equilibrium. *From the frequencies of rotational oscillation of optically anisotropic groups as observed in the Raman effect, it should be possible to determine the nature and strength of the force-fields in which they are located.* Vice-versa *if the force-fields are known, the frequencies of such rotational oscillation could be computed.* This idea again has been applied with success to a number of cases.

Since as stated above, the force-fields in which molecules or ions are located in a crystal are definite, *their translatory oscillations about their positions of equilibrium should also have exactly specifiable frequencies, determined by the masses of the particles and the strength of the fields in which they lie.* In view of the indefiniteness of the force-fields in liquids, we could hardly expect such "translatory oscillations" of the molecules or ions to be observable in the majority of fluid media. Nevertheless, in a few cases, *e.g.*, water and formic acid, they have been observed in the Raman effect as diffuse bands with small frequency shifts. The idea that such translatory movements in crystals should have well-defined frequencies is thereby strengthened. Indeed, there is observational evidence which shows that this is actually the case.

Finally, we may refer to the vibrations of lowest frequency which are essentially mass-movements and are naturally to be regarded as pertaining to the elastic spectrum of the crystal. There would be an immense number of such modes possible in a crystal which would be the more closely crowded together, the lower we go down in the scale of frequency.

Summary

An examination of the spectrograms of the Raman effect in rock-salt obtained by Rasetti reveals the existence of nine distinct Raman lines both on the Stokes as well as on the antistokes sides. The frequency shifts of these lines have been estimated. From the microphotometer record reproduced in Rasetti's paper, the relative intensities of the lines as well as the intensity ratios of the Stokes to the antistokes lines have also been evaluated. These nine frequencies have been identified as due to the nine distinct modes of vibration of the sodium chloride lattice to be expected on the basis of the Raman dynamics of crystal lattices. Though these vibrations are forbidden in the Raman effect as fundamentals, they are allowed as octaves and appear as such in the spectrum. It is pointed out that the Born theory of crystal dynamics is not capable of offering any satisfactory explanation for the observed facts.

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LUMINESCENCE SPECTRA AND VIBRATIONS IN CRYSTAL LATTICES

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1. Introduction

An extensive literature[1] has grown up on fluorescence spectra, and numerous studies of the spectra of crystals have been made in the last few years. Cooling the crystals to low temperatures (*e.g.*, that of liquid air or hydrogen) has played a great and fundamental role in these investigations. Luminescence spectra are often diffuse and blurred at ordinary temperatures, and this is usually ascribed to fluctuations in the strength of the crystalline field arising from thermal and other disturbances. On reducing the temperature, these disturbances diminish and the spectra undergo notable changes, in many cases becoming clearly resolved into narrow bands or sharp lines. Analogous changes also occur in the complementary absorption spectra when the temperature is lowered. Hence, it is usually quite essential that the luminescence and absorption spectra should be studied at the lowest available temperatures. Another important fact, as pointed out by Randall,[2] is that many ordinarily non-fluorescent solids become fluorescent at low temperatures. The belief that only a few substances fluoresce has been proved to be not quite correct, and we know to-day a fairly large number of solids giving luminescence spectra. They may, broadly speaking, be placed in one or the other of two classes.[3,4] To one class belong the uranyl salts, the platinocyanides, the rare-earth and manganese salts which fluoresce in the pure state due to the presence of an incomplete $3d$ or $4f$ shell. In the other class, the luminescence is due to the presence of impurities, as Boisbaudron[5] first pointed out, or to some internal distortion or mosaic structure in the crystal. This includes the Lenard-Klatt sulphides, alkali halides, zinc sulphide, chromium and rare-earth activated solids and diamond. The common activating impurities are Cu, Mn, Ag, Bi, Cr, Th and the rare-earth elements. In some cases the stochiometric excess of the metal (*e.g.*, in zinc oxide and the alkali halides) or exposure to X-rays also produces luminescence.

It is now well known that sharp emission spectra are not the characteristic of gases only. In fact, some polyatomic molecules give continuous

spectra in emission, while the luminescence spectra of some solids give lines as sharp as those of gaseous atoms. As Spedding[6] has pointed out, we may divide the luminescence spectra of solids into two large classes, the "continuous" and the 'discrete' or 'line' spectra. Spedding has also discussed the origin of these two types. The appearance of clearly resolved lines obviously demands that both the upper and lower states are sharp. The following solids have been known to give discrete or line spectra at sufficiently low temperatures.

1. Diamond where the luminescence is probably due to some sort of mosaic structure.[7]

2. The chromium (transition element) activated luminescent solids, *e.g.*, ruby.

3. Solids containing rare-earth elements.

4. Solids containing foreign atoms scattered through their lattices *e.g.*, the sulphide, halide and oxide phosphors, of some metals.

5. Some pure salts, *e.g.*, the uranyl compounds.

6. Organic compounds having a double bond, *e.g.*, solid benzene.

7. Solidified gases, *e.g.*, solid nitrogen.

Whether the luminescent substances are pure or impurity-activated, the importance of studying their spectra along with the complementary absorption spectra cannot be over-emphasised. At the present moment when the exploration of the energy levels of crystals is making rapid progress, such studies are of great value. Their importance is as great to-day for the understanding of the energy levels in a crystal as was the study of the band spectra of molecules, twenty years ago, to understand the energy levels in the gaseous state. The theoretical side, which has also made a considerable progress within the last thirteen years notably at the hands of Brillouin, Wilson, Peierls, Wigner, Seitz, Slater, Gurney, Mott and others, has been shaped to what is known as the "Zone theory" of the solids. Although this theory claims successfully to have explained the difference between a conductor and an insulator, yet as regards the excited states it has not been very successful. Attempts have been made to apply the theory to the case of luminescence in solids. Thus, Seitz[9] exlpains the fluorescence of zinc sulphide and alkali halide phosphors activated by thallium, while Milner[10] gives a broad outline of the difference between the pure and impurity-activated phosphors. It must be said, however, that there is, as yet, no universal mechanism known explaining the observed facts.

Still, whatever may be the mechanism of the main electronic transition, in many cases where this transition is modified by the internal vibrations

of the solid, some very important information can be procured concerning the nature of these vibrations. Such information has become of great interest in view of the recent theory put forward by Raman[11] which suggests that the thermal vibrations of the crystals are monochromatic and not continuous, as the theories of Born and Debye assume them to be. Although the Raman scattering of light in crystals usually gives some of the desired information, owing to the selection rules involved, not all the frequencies can appear as fundamentals in every case. In the present paper, an attempt is done to throw some light on the problem from the evidence gained from the literature on the luminescence spectra of solids. Wherever possible this evidence is supplemented by that gained from the corresponding absorption spectra.

2. *Diamond*

This case is of exceptional interest in view of the elementary character of the substance and the simplicity of its structure. The emission of light by diamond in various circumstances has long been familiar knowledge. Crookes and Becquerel who studied the phenomenon noticed and recorded the appearance of some lines in the green and yellow regions of the spectrum. Walter had noticed that some diamonds exibit an absorption band at 4157 Å. That a bright band appears at the same position in the luminescence of many diamonds was noticed by Ramaswamy,[12] Bhagavantam,[13] John[14] and by Robertson, Fox and Martin.[15] The subject has since been thoroughly investigated with the diamonds in the collection of Sir C. V. Raman by Nayar[16] and more recently also by (Miss) Anna Mani (1942–43) in her as yet unpublished work. By studying the phenomena at liquid-air temperatures a notable advance has been achieved in the knowledge of the spectra of diamond.

At low temperatures, the 4157 Å band shifts and appears as a sharp line or doublet centred at 4152 Å. The bright green luminescence of some diamonds is similarly associated with a sharp line at 5032 Å. The appearance of bright and dark lines with these wave-lengths respectively in emission and in absorption indicates that they represent electronic transitions. Their intensities vary enormously from diamond to diamond. These electronic transitions are found further to be associated with emission spectra showing much observable detail and extending towards longer wave-lengths in fluorescence; similar spectra extending towards shorter wave-lengths are also noticed in absorption in each case. The intensities of these spectra vary in the same way and proportionately with that of the associated electronic transition from specimen to specimen. The features observed in emission and absorption are found to exhibit

perfect mirror-image symmetry in the frequency scale with reference to the associated electronic transitions. These facts indicate that the spectra arise from combinations of crystal lattice vibrations with the electronic transitions. The observed frequency differences lie in the infra-red region of the spectrum, and the values determined from emission and absorption data agree with each other and are also the same for both the blue and the green luminescence.

The most clearly defined and accurately measurable lattice frequencies for diamond found in the studies of Nayar and of (Miss) Mani are (in wave-numbers) 1332, 1248, 1149, 1088, 1013, 935, 784 and 544, and these are probably the eight fundamental frequencies of the diamond lattice. The spectra indeed extend to both larger and smaller frequency shifts from the electronic transitions. They are, however, both feeble and diffuse towards larger frequency shifts, indicating that these are probably octaves and combinations of the frequencies listed above. Much detail is also observable and measurable in the spectral region with frequency shifts smaller than 544 $cm.^{-1}$ This region appears only feebly with the 4152 transition, but quite strongly with the 5032 transition. It is noteworthy that the highest fundamental frequency 1332 determined from these studies agrees closely with the characteristic frequency of diamond observed in its Raman spectrum. Taken altogether, the results make it clear that the vibration spectrum of the diamond lattice consists essentially of a series of discrete monochromatic frequencies and is not a continuous one.

3. *Chromium (Transition Elements) as Activator*

Most of the divalent manganese and trivalent chromium compounds give well-defined spectra. The electronic transition responsible for these is due to the rearrangement of the electrons in the incomplete 3*d* shell. Manganese happens to be the best impurity activator inasmuch as it imparts luminescence to the greatest number of cases. Randall[17] has studied the fluorescence spectra of pure manganese halides and also of the compounds activated by manganese. Kroger[18] has studied the Zn_2SiO_4 Mn_2SiO_4 mixed system. Considerations of the absorption spectra of the pure compounds of manganese by Gielessen[21] show that the electronic transition is $^2G - {}^4F$ of the Mn^{++} ion. No associations of the lattice vibrations with the electronic transion seem to have been recorded.

Deutschbein[19] has studied the chromium activated phosphors most extensively. Like chromium, the cobalt and nickel phosphors also give sharp lines both in fluorescence and absorption. It is found that chromium fluoresces in compounds where Cr_2O_3 can be isomorphous with the

bedding, *e.g.*, in ruby. Where the distortion of the lattice is greater, the spectra are more diffuse. Out of the many naturally occurring stones such as the ruby, sapphire, red spinel, etc., which emit the red fluorescence of the chromium impurity,[20] ruby has been studied most thoroughly. It is suggested that the fluorescent doublet at λλ 6927 and 6942 A° is due to the Cr^{+++} ion. Among the recent workers who have studied the fluorescence spectrum of ruby may be mentioned Venkateswaran,[22] Thosar[23] and Miss Mani.[24]

Apart from the electronic transition in Cr^{+++} ion, the part played by matrix crystal corundum has to be considered. Deutschbein was the first to explain the sharp band at λ 7138 A° ($\nu = 14006$ cm.$^{-1}$) as being due to the superposition of the Raman frequency 412 cm.$^{-1}$ of the ruby lattice on the electronic transition responsible for the band at λ 6935 A° (14416 cm.$^{-1}$). Thosar who suggested that the Cr^{+++} ion replace the Al^{+++} ion in the lattice was led to the conclusion that bands on the antistokes side of the main band must be due to the proper vibrational frequencies of the molecular group Cr_2O_3. (Miss) Mani has studied the luminescence, Raman scattering and absorption of ruby, and she finds that there is an approximate mirror-image symmetry for the bands at λλ 6595, 6693 and 6817 Å on the antistokes side and for those at λλ 7324, 7275, 7188, 7138 and 7030 on the Stokes side. With the help of three infra-red frequencies at 909, 847 and 741 cm.$^{-1}$ and two Raman frequencies at 412 cm.$^{-1}$ and 376 cm.$^{-1}$ of the Al_2O_3 lattice, she has suggested that 8 bands both on the Stokes and antistokes side could be explained.

In this connection it is worthwhile mentioning certain features of the absorption spectra of chrome-alums which have been studied by various investigators[25–29] at temperatures as low as that of liquid hydrogen. Sauer has for example studied the effect of isomorphous replacement in a group of eleven sulphate and selenate chrome alums at – 190° C. Discrete absorption is found in general in the red and orange region followed by a strong continuum with maxima approximately at λλ 5700 and 4000 A°. On lowering the temperature to that of liquid hydrogen, the continuum narrows, becomes less diffuse and often resolves into finer structure. The spectra of selenates are richer in lines than those of potassium chromium sulphate and the lines are superior in sharpness at the temperature of liquid air. Krauss and Nutting have analysed the spectra consisting of a number of lines, and they find that combinations of lattice vibrations with both upper and lower electronic states of Cr^{+++} are involved. Bands are observed in all the alums shifted about 330, 570 and 800 cm.$^{-1}$ to higher frequencies than the electronic absorption lines. Combinations of the internal oscillations of the anions are weak but have also been observed.

Here again we find definite evidence regarding the sharpness of the internal vibrations in the solid state.

4. The Rare-Earth Phosphors

The ions of rare-earths, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er and Tm give very sharp lines both in the absorption and luminiscence spectra. Such spectra are found both in the pure rare-earth salts and the solids where they are present as impurities. The lines are sharper than those obtained in the chromium activated phosphors. It is found that unlike the Cr^{+++} ion the rare-earth ions need not be isomorphous with the bedding. The spectra arise out of the transition within the shielded incomplete $4f$ shell of the ion. The levels are split up by the electric fields within the atom in accordance with the theory of Bethe.[30] Each line has therefore, companions depending on the symmetry of the crystalline field and J values of the states of the ion.

The naturally occurring fluorites were studied by Haberlandt[31] and his co-workers who recognised that the divalent rare-earth ions are responsible for the fluorescence. The pioneering work in the luminescence spectra of the rare-earths was, however, done by Tomaschek[32] and collaborators. The sharpness of the lines which resembles that of the lines in the gaseous state permits to study the influence of the surrounding field on the spectra very accurately. At Dresden a most thorough investigation of the problem has been made by what they call ' the method of line fluorescence '. Extremely useful results have been obtained regarding the nature of the crystalline fields, structure of glasses, phosphorescence centres in glasses, the hyper-structure of the crystallised substances and the constitution of liquid solutions which have been shown to have crystalline structure. It is found that the line structure of the spectra in the crystalline state is diffuse in the vitreous state. Fluorescence of the pure salts and their solutions has also been studied[33, 34] and recently Chatterji[35] has given the interpretation of the fluorescence spectra of artificial fluorites activated by the rare earth elements.

Tomaschek[36] has discussed the known facts regarding the line spectra of solid solutions in emission and absorption, particularly those of the rare earths in a separate paper. According to him the spectra represent electronic jumps on which are superposed the vibrations of the parent lattice and the light centre itself. The vibrations thus obtained are of lower frequencies than those obtained from the Raman effect of the parent lattice. This difference is explained on the assumption that the rare-earth molecules may act as inert loads. If this explanation is correct the changes of frequency should be greater the larger the rare-earth and smaller the bedding molecule. This point has been experimentally confirmed. For example, the praseodymium

ion which produces a greater change of frequency than the samarium ion has a diameter 3 per cent. greater than that of the latter. On the other hand, barium oxide has a larger diameter than calcium oxide and the change of frequency produced by bedding samarium in it is much less. Diagrams are given by Tomaschek to show how the lattice frequencies of alkaline earth sulphides and oxides compare with those obtained from the fluorescence spectra when samarium and praseodymium are embedded in them. Tomaschek has further shown that similar lattices give similar spectra and that crystal type has a great influence on them. Leaving aside the mechanism of electronic transition, the position can be summed up by saying that frequencies characteristic of the matrix lattice modified by the presence of the rare-earth ion in question are found in the spectra of rare earth phosphors. These frequencies are associated with the electronic transition in the ion and surely, there cannot be the least doubt about the monochromatism of these lines.

In the following, the foregoing remarks will be supplemented with evidence gained from the experiments on the absorption spectra of some crystalline rare-earth salts. These spectra again consist of sharply defined and widely spaced groups of bands. The separate groups owe their origin to the decomposed multiplet levels by the electric fields. The electronic transition again arises out of the rearrangement within the 4f configuration of the rare-earth ion.[37] A good amount of work has been done by Spedding[38] and others who find that low lying levels (electronic) are to be observed in $Nd_2(SO_4)_3\,8H_2O$; $NdCl_3\,6H_2O$, $Pr_2(SO_4)_3\,8H_2O$ and the europium salts. But to account for the large number of lines it is necessary to couple internal vibrations of the crystal with the electronic transition. The work of Ewald,[39] Howe and Herbert[40] and Weissman and Freed,[41] however, demands greater attention here, for it gives some definite evidence regarding the vibrations in the rare-earth crystals.

Taking very thick layers of neodymium salts Ewald found that each group of electronic transitions is accompanied by faint lines, spaced in the same manner on the short wave-length side. The spacing in the weak lines is found to be the same in each group. In the case of the mixed nitrate $3\,Mg(NO_3)_2\,2Nd(NO_3)_3\,24H_2O$ these frequencies correspond to the vibrations of the NO_3^- ion and the H_2O molecule. On replacing the water of crystallisation by heavy water, vibrations corresponding to that of D_2O are observed. Ewald also found that some low frequencies from 50 $cm.^{-1}$ to 200 $cm.^{-1}$ represented lattice vibrations; for an increase in the mass of the lattice atoms effected a decrease in the frequencies. Hellwege[42] by the restrahlen method found that these were actually the crystal oscillations.

Striking results are obtained by Freed and Weissman in the corresponding salt of europium. The spectrum, remarkably enough, consists of sharp lines even at room temperatures. They also find that in addition to the lattice oscillations on the short wave-length side of the electronic frequency, there appears a similar pattern of lines towards the longer wave-lengths displaced by an equal amount in frequency. On lowering the temperature, these new lines vanish; thus indicating that they are thermal oscillations of the lattice and that their presence in the spectrum corresponds to the anti-stokes frequencies in Raman effect. These authors also give evidence to show that crystal structure continues even in the solution state of the salt. But the lines are naturally more diffuse there.

The observations of Weissman and Freed appear to have a great significance from our point of view. The results show that the vibrations of the solids are (at least in the observed case) sharp even at room temperatures. It seems plausible that the diffuseness in any observed spectra is mainly due to the electronic transition, the thermal vibrations remaining still sharp.

5. Fluorescence Spectra of Impurity Activated Solids

A greater number of solids fluoresce only in the impure state. The chief characteristic of their luminescence spectra is the lack of resolution even at low temperatures. On this account, nothing much has been said from the theoretical point of view. The alkali halide phosphors have been studied by a number of investigators, notably by Pohl, Hilsch and others.[43] The absorption bands by which luminescence may be stimulated, consist of several sharp peaks near λ 3000 Å to the short wave-length side and are characteristic of such phosphors. They are, however, absent in the pure halides. The luminescence lies in the near ultra-violet and visible region. Von Hipple[44] has given a theory of these phosphors. Zinc sulphides give broad bands depending on the nature of the impurity atoms.[45] Reference to Seitz's theoretical discussion in this connection has already been made.

From the experimental standpoint the resolution of the broad, featureless bands in many impurity activated phosphors has been attempted by Schmidt,[46] Schellenberg[47] and Howes[48] but much success has not been obtained. Recently, however, Ewles[3] has done some valuable work in this direction and here, his results will mainly be quoted. He obtained the most remarkable resolution of the ultra-violet bands of CaO phosphors, into almost line-like components with cathode ray excitation. This condition was obtained by cutting down the cathode ray current to a fraction of a micro-ampere by running the machine very slowly or by putting a spark gap in parallel with the tube. The spectrum obtained in the ultra-violet

region appears to be divided into a number of groups of broadened lines each suggesting a band group. The bands in the visible region are however broad.

In CaO, for example, two groups of bands are observed. They are named as (F, G) and (H, K, L) groups. The bands can be represented by a formula of the type

$$\nu = \nu_e + (v' + \tfrac{1}{2})\,\omega' - (v'' + \tfrac{1}{2})\,\omega''.$$

The following table gives the bands of the (F, G) group.

TABLE I

Bands in the F, G Group of CaO

Designation	Observed	Calculated	v',/v''
F	27404	27404	0, 0
G	27166	27160	1, 1
F_1	26891	26896	0, 1
G_1	26647	26652	1, 2
F_2	26385	26388	0, 2
G_2	26142	26144	1, 3
F_3	25886	25880	0, 3

$\nu_e = 27526$ corresponds to the electronic transition:

CaI $4s4p\ 3P^\circ - 4s\ 4d\ {}^3D$, $\omega' = 244$ cm.$^{-1}$ and $\omega'' = 508$ cm.$^{-1}$ Similarly for the (H, K, L) group $\nu_e = 25816$, and $\omega' = 294$ cm.$^{-1}$ and $\omega'' = 493$ cm.$^{-1}$

The frequencies 508 cm.$^{-1}$ and 493 cm.$^{-1}$ are presumably the same as 453 cm.$^{-1}$ the maximum vibrational frequency of the CaO lattice as given by Tolksdorf.[49] Further evidence that the CaO crystal plays a predominant part in the emission of the (H, K, L) group is given in favour of this assumption.

Fourteen samples of CaO phosphors, one pure and 13 impurity activated have been examined both with cathode ray and ultra-violet excitation. It appears that the activators merely determine the relative intensities of a set of groups but the positions are determined by the lattice itself. The results obtained with CaO are confirmed by working with other sulphides and oxides. In the case of SrO a set of 4 broadened lines is obtained which can be put in the equation,

$$\nu = 26410 + (v' + \tfrac{1}{2})\,\omega' + (v'' + \tfrac{1}{2})\,404 \text{ cm.}^{-1}$$

For ZnO, similarly,

$$\nu = 26764 + (v' + \tfrac{1}{2})\,322 - (v'' + \tfrac{1}{2})\,571 \text{ cm.}^{-1}$$

The frequencies 404 cm.$^{-1}$ and 322 cm.$^{-1}$ are probably due to the SrO and ZnO lattices. The results of other previous workers have been explained on similar lines. Although the evidence regarding the part played by the

crystal frequencies is not very conclusive, the review shows that, at the liquid-air temperature, well resolved, broadened lines presumably due to the lattice vibrations have been obtained. It would be of interest to study these spectra at temperatures even lower than this. Even here, it is highly interesting to note that the spectra which previously were known to consist of broad featureless bands have been resolved into line-like appearance.

6. The Uranyl Compounds

It is well to emphasise the dependence of luminescence spectra on crystal structure.[50] The uranyl salts and the platinocyanides, which are two striking examples of complex co-ordination groups, greatly owe their property of luminescence to the crystalline state. Levy,[51] for example, found that out of the three pure samples of Ba Pt $(CN)_4 4H_2O$ only two, which were crystalline, gave fluorescence. In uranyl compounds also, Nichols and Howes[52] find that the characteristic spectra can only be obtained in the crystalline state. Even in substances where uranium acts as impurity activator, well-resolved spectra at liquid-air temperatures have been obtained only if the matrix substance is in the crystalline form.[53] It is interesting to see that the fluorescence study of uranyl compounds in the crystalline state gives much information regarding the nature of vibrations in the solid.

Fluorescence is the property of uranyl compounds only; the uranium salts do not show any luminescence. At room temperatures, the pure salts fluoresce giving rise to nearly 8 rather broad and diffuse regularly spaced bands in the green-red region. These become sharp and get resolved into lines at the liquid-air temperature. At the liquid hydrogen temperature the lines have been reported to become as fine as those of a spark spectrum. Table II gives the wave-number values of the lines in the fluorescence spectrum of uranyl fluoride at the liquid air temperature taken by Mr. N. D. Sakhwalkar in this laboratory.

TABLE II

The fluorescence Lines in $UO_2F_2 \cdot H_2O$

Series	Group					$\Delta\nu$ (average)
	1	2	3	4	5	
A	20237 (w)	19360 (d)	18503 (d)	17641 (w)		865 cm.$^{-1}$
B	20083 (s)	19218 (s)	18354 (s)	17493 (m)	16740 (w)	861 cm.$^{-1}$
C		19152 (d)	18293 (d)	17429 (m)	16577 (m)	858 cm.$^{-1}$
D		19126 (d)	18270 (w)			856 cm.$^{-1}$

s = strong d = dim
m = medium w = weak

This is the simplest fluorescence spectrum to be found in the uranyl salts. Measurement of the lines is very approximate; still it will be seen that the spectrum consists of 5 groups each separated from the next one by 860 cm.$^{-1}$ This separation of 860 cm.$^{-1}$ is characteristic of all the spectra. Dieke and Van Heel,[54] therefore, suggested that the electronic transition is due to the uranyl ion and that the jump is modified by the oscillation frequency 860 cm.$^{-1}$ of the UO_2 group. Van Heel[55] drew up the energy level diagrams to explain the spectrum, but a really satisfactory explanation has not yet come forward.

The Raman spectra of the UO_2^{++} ion in solution were obtained by Conn and Wu[56] and Satyanarayana.[57] It is confirmed that the 860 cm.$^{-1}$ frequency is due to the symmetric (U=O) vibration. Two more frequencies at 930* cm.$^{-1}$ and 210 cm.$^{-1}$ correspond to the antisymmetric and the deformational vibrations of the bent UO_2^{++} molecule. In addition to these, certain companions of these vibrations have also been obtained which are due to the undissociated uranyl compound. Taking these facts into account and treating UO_2^{++} molecule as a triangular one, the author has found it possible to explain the spectra more or less completely with due regard to the intensities of component lines of each groups.

The absorption spectra again consist of sharp bands spaced at intervals of 700 cm.$^{-1}$ This is obviously the vibrational frequency in the excited state of the uranyl ion corresponding to 860 symmetric valence vibration of the ground state. Thus, the uranyl ion, as far as the vibrational energies are concerned, behaves more or less as a free gaseous molecule in the crystalline uranyl compounds and gives rise to extremely sharp bands in the luminescence spectra which are mostly due to the vibrations of the ion.

1. Solid Benzene

Investigations of the Raman spectra of crystals probably first revealed the sharpness of the infra-red vibrations; attention to this was drawn as early as 1929.[58] Some solids such as ice, salts having SO_4^{--}, NO_3^-, *etc.*, as radicals show, that vibrations corresponding to the molecule or the radical in question do exist in the solid. The luminescence and absorption spectra which have been described above show that similar vibrations exist in the luminescent solids and are as sharp and discrete as in the gaseous state. Some more evidence obtained from the study of fluoresence and absorption of C_6H_6 will now be given to show that vibrations corresponding to the gaseous state also present themselves in the solid state.

* Observed in the infra-red absorption spectrum of the uranyl salts in crystalline state by Conn and Wu.

The fluorescence spectrum of benzene has been investigated both in the gaseous[59] and the solid state.[60] The fluorescence spectrum of solid benzene at − 185°C. consists of two progressions F, E, D, C, B and *e*, *d*, *c*, *b*. The interval between F–E or *e*–*d* is 990 cm.$^{-1}$ and that between *e*–E is ~600 cm.$^{-1}$ These bands become extremely sharp at the liqud hydrogen temperature. For, the structure of the bands, instead of splitting up, completely disappears at this low temperature and only the maxima are left. It is remarkable that the fluorescence spectrum of the solid benzene closely agrees with series II fluorescence progression of the vapour state (Table III). The equation for this series is given as $\nu = 39000 - 1000n - 163p$.

TABLE III

Fluorescence Spectra of Solid and Gaseous Benzene

n / *p*	2		3		4		5		6	
	Vapour	Solid	Vapour	Solid	Vapour	Solid	Vapour	Solid	Vapour	Solid
0	2675		2749		2825	2822	2907	2904	2996	
1	2686	2686	2759	2756	2838	2834	2920	2921	3007	3008
2	2698	2695	2772	2772	2851	2853	2933	2935		
3	2710	2712	2785	2785	2864	2868	2948	2956	3038	
							2950			

The absorption spectra of benzene and the substituted benzenes have also been studied both in the vapour state[61] and solid states.[60] Due to the great advance achieved in the understanding of the polyatomic spectra in recent years, it has been possible to give a rather complete explanation of the observed absorption spectrum of benzene.[62] The solid benzene at −180° C. shows the presence of very strong progression, with a spacing of 923 cm.$^{-1}$ in the spectrum. This is similar to that observed in the gaseous state. The weaker progression of the gaseous benzene with a spacing of 505 cm.$^{-1}$ is, however, absent in the spectrum of the solid benzene. The latter is again shifted by 261 cm.$^{-1}$ to the red. A complete explanation for the observed bands has been given except for some weaker bands spaced at intervals of nearly 60 cm.$^{-1}$ which are probably due to the superposition of the crystal frequencies. For, they cannot be due to the rotational energy which will not exist at such low temperatures.

It will be noted that the frequencies 990 cm.$^{-1}$ and 922 cm.$^{-1}$ are the totally symmetric vibration frequencies of the C–C bond in the ground and the excited states. This case is exactly similar to that already mentioned in the case of uranyl compounds. The 606 cm.$^{-1}$ and 520 cm.$^{-1}$ again are the C vibrational frequencies in the ground and the excited states.

It is not necessary to give a further account of the fluorescence and absorption spectra of other organic molecules. It is known that an unsaturated or resonating band in organic compounds generally gives rise to discrete spectra. For, when a double bond exists, one of the electrons can be excited without destroying the bond and this accounts for the sharp levels.

8. *Solid Nitrogen*

In 1924 Vegard[63] discovered that when solid nitrogen was bombarded by cathode rays it emitted a radiation, the spectrum of which consisted of sharp bands and lines. He extended his work considerably and the spectra of solid nitrogen, nitrogen-argon mixtures in various proportions and so on, at the temperatures of liquid hydrogen and helium, were studied by various types of excitations, *e.g.*, slow and swift cathode rays, canal rays, X-rays etc.[64] A considerable number of spectra were thus studied and the numerous lines and bands were classified into series and systems of such series. It is not possible to give all the details regarding these; in brief it may be said that they can be represented by equations of the type

$$e.g.,\ \nu_\delta = 21245{\cdot}5 - 1631{\cdot}1n + 10{\cdot}7\,n^2$$
$$\nu_\theta = 22976{\cdot}1 - 1633{\cdot}1n + 11{\cdot}3\,n^2$$

for the δ and the θ series respectively. Other types of series which are characteristic of the solid state (for they appear in the phosphorescence emission) can be represented similarly but the spacing between the successive bands is larger here,

$$e.g.,\quad \nu_\xi = 17232 + 2231{\cdot}5\,n + 7{\cdot}4\,n^2.$$

Series D, α, χ, ξ and ϵ are similar so far as the spacing between the successive bands is concerned. The nature of the equations clearly shows that the series are due to an electronic transition modified by a vibrational frequency which combines with it in various quanta. The ϵ series which is of greatest importance, involves vibrational frequencies of the excited as well as the ground states of the electronic transition.

Thus,

$$\epsilon\,(m_1, m_2) = \nu_0 + \mathrm{T}_2\,(m_2) - \mathrm{T}_1\,(m_1)$$

where m_1, m_2 correspond to the upper and the lower levels of the crystal. T_2 and T_1 are approximately vibrational frequencies of the excited and the ground states respectively; for $\mathrm{T}_2\,(m_2) = 1453{\cdot}1\ m_2 - 14{\cdot}866\ m_2^2$ and $\mathrm{T}_1\,(m_1) = 2323{\cdot}3\ m_1 - 14{\cdot}898\ m_1^2$.

Experiments showed that the solid nitrogen has two allotropic modifications ; the α-form which exists below 35·5° K. and the β-form which

exists above this transition point. While both the forms give luminescence on excitation with the cathode rays, it is only the α-form that gives the after-glow (phosphorescence). The D, α, χ, ξ and ϵ series which appear in the after-glow spectrum are thus the typical bands of the solid form. Vegard explained the non-appearance of the after-glow in the β-form by assuming that the electronic transition, which is a forbidden one, appears in the α-form because the molecular axes are fixed in the lattice (which is cubic).[65] In the β-form, however, the axes are absent because the molecule rotates.[66] This, however, does not explain the decaying property of the after-glow which does not obey the exponential law. It was, therefore, assumed that the bombarding rays produce dissociation of the molecules into atoms. The latter recombine to form an excited molecule by the force of some chemical energy.

The then existing facts were all in agreement with the assumption that the electronic transition is of the forbidden type. The level $A^3\Sigma$ of the N_2 molecule was known to exist from the analysis of the first positive nitrogen bands. This level is metastable with respect to the ground $X^1\Sigma^+_g$ state. The vibrational levels of the ground and the excited states were known to be of the values of 2359·6 cm.$^{-1}$ and 1460·4 cm.$^{-1}$ [67] respectively. However, the discovery of the Vegard-Kaplan bands of N_2 by Kaplan[68] (transition $A^3\Sigma_u^+ - X^1\Sigma_g$) completely removed the last traces of doubt. The ϵ bands now correspond to the above transition[69] and vibrational energies T_1 and T_2 correspond to the vibrational frequencies of the $^1\Sigma^+$ and $^3\Sigma$ states respectively.

Lastly, Vegard finds that the series are not composed of single lines but of two or more components. The splitting up is more pronounced at the liquid helium temperature than at that of liquid hydrogen. The multiplicity cannot be due to the rotational energy for obvious reasons. Excepting for the α-series which has a splitting of 69 cm.$^{-1}$ other series show a difference of 40 cm.$^{-1}$ between the successive components. Vegard suggests that these are due to the change of vibrational energy of the molecular element in the crystal lattice.[70] In other words, these are the oscillation frequencies of the lattice.

Here again we have strong evidence to show that thermal frequencies existing in the solid state are sharp and monochromatic. Further, it has once again been shown that the vibrational energy of the molecule remains more or less the same both as regards monochromatism and frequency in the gaseous and the solid states. A little difference, if at all, has to be expected due to the Van der Waals forces.

Summary

A general survey of the known luminescence spectra of crystals is given. Those which give discrete spectra have been divided into seven classes. The luminescence spectrum of each of these crystals is examined to see what evidence it gives regarding the nature of the vibrations in the crystal lattices. Wherever possible the information thus obtained is supplemented by the evidence furnished by the complementary absorption spectra. It is shown that there is a mass of striking evidence indicating that vibrational frequencies are sharp and monochromatic in all crystals. Those luminescence spectra, which are not discrete are due to an electronic transition in which one or both the electronic states involved are not sharp and hence no evidence regarding the vibrational frequencies can be gained from them. It is remarkable that over the whole range of crystal structure—from the typical covalent crystal diamond to the typical Van der Waals crystal solid nitrogen—the vibrational frequencies are all sharp and monochromatic. The ionic crystals, *e.g.*, the uranyl salts are also no exception to this rule. In many crystals some of the constituents, *e.g.*, N_2 in solid nitrogen, C_6H_6 in solid benzene, the UO_2^{++} molecule in uranyl salts and so on, behave as if they are in the gaseous state. For example, the vibrational frequency observed in the fluorescence spectrum of solid benzene at very low temperatures is thus the same as that of the ground state of the C_6H_6 molecule, probably the only difference being that the observed bands are more discrete in the crystal state owing to the absence of the rotational lines.

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CHARACTER TABLES FOR THE ATOMIC VIBRATIONS IN SOME CUBIC CRYSTALS

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1. *Introduction*

In an earlier paper in this symposium, a general group-theoretical method for dealing with lattice vibrations has been indicated. It has been shown that the solution of the normal vibration problem depends upon a knowledge of the character tables for some point groups which are associated with the different vectors* of the translation group. In the present paper it is proposed to indicate the applications of that method to four crystals of the cubic system, *viz.*, zincblende, diamond, fluorspar and rock-salt. A complete analysis of the normal modes of these and other crystals has already been given in an earlier paper of this series, basing the discussion on purely intuitive geometric principles. Hence a group-theoretical disoussion of simple cases like the vibrations of a simple cubic lattice, simple face-centred lattice, body-centred lattice, etc., is not needed here. To illustrate the principles, we propose here to put down the appropriate character tables and the nature of the normal modes for the four crystals mentioned above. All the cases considered here have a face-centred structure. The eight possible vectors for this case fall into three distinct sets, as is evident by a very simple application of the symmetry operations. The (1, 1, 1) vector forms a set by itself and (1, −1, −1); (−1, 1, − 1); (− 1, −1, 1) another set. The remaining four vectors, (−1, −1, −1); (− 1, 1, 1); (− 1, 1, 1) and (1, 1, − 1) form a set by themselves and each can be carried over into the others by the symmetry operations. Thus the interesting feature in the face-centred system is that (−1, −1, −1) becomes equivalent to the other three. We now investigate these three cases separately.

2. *Rock-salt, Zincblende, Diamond and Fluorspar Lattices*

All these cases can be dealt with by the same methods. In the rock-salt lattice, we have two non-equivalent atoms in the positions:

	Na (0, 0, 0);	Cl: $(\frac{1}{2}, 0, 0)$.
For zinc sulphide,	Zn: (0, 0, 0)	S: $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$.
For diamond,	C: (0, 0, 0)	C: $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$.
For fluorspar,	C: (0, 0, 0)	F: $(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$ and $(\frac{\bar{1}}{4}, \frac{\bar{1}}{4}, \frac{\bar{1}}{4})$.

* For an explanation of this symbology reference should be made to the previous paper.

So far as the symmetry group is concerned, it is O_h for all cases except ZnS, and excepting the centre of inversion, all the other operations, forming the group T_d, can be located at a lattice point and this feature is common to all the four cases given above. Zinc sulphide has no centre of inversion, while for rock-salt it can be located at either Na or Cl atom, for diamond at $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ and for fluorspar at (0, 0, 0). This shows that the normal modes of all the cases given above can differ only with respect to the centre of inversion. Each of the 8 possible vectors will now be taken up one by one and the normal modes evaluated by the methods fully explained in the earlier paper.

(1, 1, 1) *Vector.*—This is left invariant by all the operations of the point-group symmetry. Excepting the case for ZnS, which has T_d symmetry, the others have O_h symmetry and the reduced character of the operations is easily found when acting on the non-equivalent dynamical variables in each unit cell.

$$n_i = \frac{1}{N} \Sigma \psi (R) \chi^i (R)$$

	E	$3C_2$	$8C_3$	6σ	$6S_4$	i	3σ	$8S_6$	$6C_2$	$6C_4$	n_i (NaCl)	n_i (C)	n_i (ZnS)	n_i (CaF_2)
A_{1g} ..	1	1	1	1	1	1	1	1	1	1	..	..	..	..
A_{2g} ..	1	1	1	−1	−1	1	1	1	−1	−1	..	..	..	..
E_g ..	2	2	−1	0	0	2	2	−1	0	0	..	..	..	..
F_{1g} ..	3	−1	0	−1	1	3	−1	0	−1	1	..	1	..	..
F_{2g} ..	3	−1	0	+1	−1	3	−1	0	+1	−1	..	..	..	1
A_{1u} ..	1	1	1	1	1	−1	−1	−1	−1	−1	..	..	..	..
A_{2u} ..	1	1	1	−1	−1	−1	−1	−1	+1	+1	..	..	..	..
E_u ..	2	2	−1	0	0	−2	−2	1	0	0	..	..	..	..
F_{1u} ..	3	−1	0	−1	1	−3	1	0	1	−1	..	..	..	..
F_{2u} ..	3	−1	0	1	−1	−3	1	0	−1	1	2	1	2	2
NaCl ψ ..	6	−2	0	2	−2	−6	2	0	−2	2				
Diamond ψ	6	−2	0	2	−2	0	0	0	0	0				
Zn S ψ ..	6	−2	0	2	−2	..	..	..	..	..				
CaF_2 ψ ..	9	−3	0	3	−3	−3	+1	0	−1	1				

The last four rows give the reduced character ψ of the operations when acting on dynamical variables of the four crystal lattices. The difference in the location of the inversion in NaCl and diamond is reflected by the fact

that in the former all the six modes are anti-symmetric with respect to inversion, while in the latter they separate out into symmetric and anti-symmetric modes. ZuS has no inversion and its six modes occur in F_{2u}. For CaF_2, the mode F_{2g} gives one triply degenerate normal mode symmetric with respect to inversion while two other modes with degeneracies 3 each come under F_{2u}. If we exclude translations, these give, as is at once evident from the character table, the following frequencies:

	Degeneracy
(1) An oscillation of the sodium lattice against the chlorines in NaCl	3
(2) A mutual oscillation of the interpenetrating lattices in diamond	3
(3) A mutual oscillation of the zinc and sulphur lattices against one another in ZnS	3
(4) An oscillation of the Ca and F ions in CaF_2 which is symmetric with respect to inversion (F_{2g}). Since the inversion is located at the calcium atoms, they must be at rest in this mode	3
(5) A combined oscillation of all the calcium and fluorine atoms which is totally antisymmetric with respect to inversion (F_{2u}). The translations also occur in F_{2u}. Hence the only possibility left is that the fluorines go one way and the calciums go the other way	3

This rigorous analysis can be compared with the treatment given in an earlier paper.

$(-1, -1, -1)$ *vector referred to rhombohedral axes.*—The vectors $(-1, 1, 1)$; $(1, -1, 1)$; and $(1, 1, -1)$ referred to rhombohedral system are equivalent to $(-1, -1, -1)$ and so there is a minimum degeneracy of 4 for frequencies of this set. We consider the $(-1, -1, -1)$ vector only.

The symmetry operations keeping this invariant form the group D_{3d} in all cases except ZnS where it is simply C_{3v} without the inversion. The analysis is similar to the earlier treatment.

For ZnS, the appropriate character table consists of the first three columns and first three rows only. The distribution of frequencies in rock-salt and diamond is similar, with degeneracies 1, 2, 1, 2. The former two are symmetric with respect to inversion while the latter two are antisymmetric. Since ZnS has no centre of symmetry to distinguish the modes, we get a coupling between these two sets, which can be resolved only by forming the potential energy. For CaF_2 there are two frequencies with degeneracies

	E	$2C_3$	3σ	i	$2C_3 \times i$	$3\sigma \times i$	n_i (Nacl)	n_i (C)	n_i (ZnS)	n_i (CaF_2)
A_{1g} ..	1	1	1	1	1	1	1	1	2	1
A_{2g} ..	1	1	−1	1	1	−1	..	..	..	..
E_g ..	2	−1	0	2	−1	0	1	1	2	1
A_{1u} ..	1	1	1	−1	−1	−1	1	1	..	2
A_{2u} ..	1	1	−1	−1	−1	1	..	..	..	..
E_u ..	2	−1	0	−2	1	0	1	1	..	2
(NaCl) ψ ..	6	0	2	0	0	0				
(Diamond) ψ ..	6	0	2	0	0	0				
(ZnS) ψ ..	6	0	2	..	..	..				
(CaF_2) ψ ..	9	0	3	−3	0	−1				

1 and 2 respectively which are symmetric with respect to the inversion. On the other hand, there are four frequencies with degeneracies 1, 2, 1, 2 and antisymmetric with respect to inversion. There is a coupling here between the two single frequencies, with a similar coupling for the double modes.

The symmetry characters of the modes are at once evident from the character table. Those under A_{1g} are totally symmetric with respect to (x, y, z) and for a state of vibration represented by the $(-1, -1, -1)$ vector, this can only be in a direction normal to the (111) planes. All the normal co-ordinates of an atom 'r' involve the term $x_r + y_r + z_r$. For rock-salt, this is a vibration of the (111) planes. Being symmetric with respect to inversion, the sodiums are at rest, and alternate (111) planes of chlorine atoms move oppositely and normal to themselves. The same description holds good for the diamond lattices. For zincblende, alternate (111) planes contain zinc and sulphur atoms respectively, and the exact relative magnitude through which they move depends upon the forces between them. Hence they occur coupled together with two frequencies under A_{1g}. In fluorspar a similar motion of (111) planes occurs except that the calciums must be at rest in A_{1g} because of the symmetric nature with respect to inversion.

Coming to A_{1u} the modes of rock-salt are the same as the above case for A_{1g} except that it is the chlorine atoms which are at rest, with the sodium atoms moving. Diamond has a similar vibration which is now antisymmetric with respect to inversion. Alternate (111) planes now go two against two, thus $+ + - -$, etc. For zinc sulphide, there is no distinction between A_{1u} and A_{1g}, while for fluorspar we have two coupled modes both antisymmetric with respect to inversion. This is natural, since a motion with

the two fluorines going the same way leaves a twofold option for the calcium atom. Either the calcium can move in the same way or opposite way with respect to fluorine. Thus F Ca F or F Ca F are possible and both are antisymmetric with respect to the inversion at the calcium atom.

The representations E_{2g} and E_{1u} are double. It is easily seen from the group characters that they involve co-ordinates like $x_r - y_r$, $y_r - z_r$ or $z_r - x_r$ of an atom. They involve motions of the (111) planes in two directions in their own planes and these two directions are equivalent. For rock-salt, the same motion as described earlier takes place with either the chlorines at rest or the sodiums at rest. Alternate (111) planes move tangentially and in opposite phases in this motion. For diamond also, a similar motion takes place, and it is either symmetric or antisymmetric with respect to inversion. In the former case the alternate planes move as $+ - - +$ and in the second case they move as $+ + - -$, etc. In zincblende alternate (111) planes of the same sort move in opposite phases tangentially. As there is no inversion to distinguish the modes further, we get a coupled mode or E_g. In fluorspar, E_g gives a doubly degenerate mode which is uncoupled with any other. It is symmetric with respect to inversion and so calciums must be at rest with the fluorines going in opposite ways. Here also alternate (111) planes of fluorines move tangentially. For CaF_2 we get in E_u two coupled modes with degeneracy two each. As explained for the case of A_{2u}, this is natural, as the calcium atoms can move in the same or opposite ways with respect to the fluorines. The direction of motion however is tangential here unlike A_{2u}. This completes a description of all the modes for similar motions occurring for $(1, \bar{1}, 1)$ $(1, 1, \bar{1})$ and $(\bar{1}, 1, 1)$ planes corresponding to the three other vectors. Thus we get an extra degeneracy of four for every frequency belonging to $(-1, -1, -1)$. The distribution for this branch can hence be represented as

(1) Rock-salt:	Distinct frequencies with degeneracies		4, 4, 8, 8
(2) Diamond	,,	,,	4, 4, 8, 8
(3) Zincblende	,,	,,	4, 4, 8, 8
(4) Fluorspar	,,	,, 4, 8,	4, 4, 8, 8

We now turn to the final vector $(1, -1, -1)$. A detailed description of the geometric modes for this vector can be given as above, but we content ourselves here by merely indicating the character table and the number of the appropriate normal modes with their degeneracies. This vector is left invariant by the elements

(i) the identity;

(ii) the three two-fold rotations about the x, y and z axes, $3C_2$;

(iii) a reflexion σ_1 in a plane passing through x axis and bisecting the other two;

(iv) the products of σ_1 with $3C_2$ *i.e.*, $3C_2\sigma_1$.

This is the symmetry group D_{2d} for a crystal with no centre of inversion such as ZnS. The addition of a centre of inversion in rock-salt and fluorspar brings in eight operations more $D_{2d} \times i$ and the total group is of order 16. In diamond, however, the inversion does not commute with all the operations in D_{2d}, particularly the three twofold rotations P_1, P_2, P_3 about the three cubic axes. Its association with these elements brings in translation operations thus

$$i P_1 i^{-1} = P_1 \tau_x \text{ or } i P_1 i^{-1} P_1^{-1} = \tau_x, \tag{2}$$

Since $i^{-1} = i$ and $P_1^{-1} = P_1$ this can be written as

$$(iP_1)^2 = \tau_x;\ (iP_2)^2 = \tau_y;\ (iP_3)^2 = \tau_z. \tag{3}$$

Hence the space group keeping the vector $(+1, -1, -1)$ invariant in diamond lattice cannot be resolved as the product of a point group and a translation group. The simplified formula (17) in the paper on general theory is not directly applicable here and we have to derive the full character table for the space group. All these complications can be avoided, if, for a moment, we regard the two non-equivalent atoms in diamond as being different. Consequently there will be no centre of inversion here and the pattern is exactly the same as for ZnS. Afterwards, when the normal modes for ZnS are written down, we can, if we choose, bring in the inversion and easily see what modification it can bring in the normal modes.

	E	P_1	P_2, P_3	$\sigma_1, \sigma_1 P_1$	$P_2\sigma_1, P_3\sigma_1$	n_i
A_1 ..	1	1	1	1	1	..
A_2 ..	1	1	1	−1	−1	..
B_1 ..	1	1	−1	1	−1	2
B_2 ..	1	1	−1	−1	1	..
E ..	2	−2	0	0	0	2
ψ ..	6	−2	−2	2	−2	..

We thus have two single modes (coupled) and two double modes (coupled). If the inversion is now introduced, the coupling is removed with the modes separating out according as they are, or are not, symmetric with respect to inversion. We have here a process of building up the representations of a group from its subgroups. The full method is explained in the paper on general theory. Since the inversion brings in the translations,

we first choose the group $D_{2d}\times$ translations for diamond. According to Clifford's work each representation of this group we need here, is merely the direct product of the representations for D_{2d} and the representation (1, −1, −1) of the translation group.

Here $$\chi(\tau_x) = -\chi(\tau_y) = -\chi(\tau_z) = 1 \qquad (5)$$

Hence $$\chi(P_1\tau_x) = \chi(P_1);\ \chi(P_2\tau_y) = -\chi(P_2);\ \chi(P_3\tau_3) = -P_3 \qquad (6)$$

for all representations associated with this vector. We now append the inversion and derive the group table for $D_{2d} \times \{E, i\}$. Taking the representation B_1 it is easily seen that it is sent into the representation A_1 by the inversion. This is because the inversion changes P_1, P_2, P_3 into $P_1\tau_x$, $P_2\tau_y$ and $P_3\tau_z$ the characters for which, however, are equal to $\chi(P_1)$, $-\chi(P_2)$ and $-\chi(P_3)$ from (6).

Thus $$\chi(P_1) \rightarrow \chi(P_1) \qquad \chi(P_2) \rightarrow -\chi(P_2) \qquad \chi(P_3) \rightarrow -\chi(P_3)$$

as a result of the inversion. Thus A_1 and B_1 are equivalent under the inversion and they give rise to a double representation in the space group. The degeneracy of the mode under B_1 is thus increased and as a consequence the coupling is removed. The representation E however is left invariant by the inversion and so we do not get any new combination of representations. This gives rise to two representations in the space group, one which is symmetric, and the other antisymmetric with respect to inversion. Accordingly, the distribution of the six normal modes in diamond lattice for this vector is 2, 2, 2. From the symmetry characters of A_1, B_1 and E the normal modes can be derived. They will be found to be identical with the descriptions given earlier.

For fluorspar and rock-salt, the inversion is also located at a lattice point and so commutes with the point group D_{2d}. Hence there is no need to bring in a space group, and the appropriate character table is given by the direct product of D_{2d} and the inversion group with two representations $\chi(i) = \pm 1$. The further analysis is then exactly the same as above and there is no real need to put it down here again. The distribution of the modes is the same as given in the earlier paper.

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Summary

In this paper, the character tables for groups associated with vectors defining normal modes are given for four cubic crystals based on a face-centred Bravais lattice, *viz.*, rock-salt, diamond, zincblende and fluorite. The method of deriving normal modes from these tables, described in an earlier paper, is illustrated here.

THE FREQUENCY SPECTRUM OF THE DIAMOND LATTICE

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1. Introduction

The many remarkable physical properties which diamond exhibits and the fact that the element carbon of which it is a crystalline form occupies a unique position in the field of chemistry invest this substance with an altogether exceptional interest for the experimental physicist. There is good reason why the mathematical physicist should also regard diamond with special interest. It is the typical valence crystal, and as it belongs to the cubic system and has a relatively simple structure, its physical behaviour should be readily amenable to theoretical explanation and computation. Indeed, the diamond lattice may fairly be regarded as a test case for any theory of the solid state.

Ramaswamy (1930) observed a sharp and intense line with a frequency shift of 1332 cm.$^{-1}$ in the Raman spectrum of diamond and interpreted the same as the "rest-strahlen frequency" of diamond. He established the correctness of this interpretation by showing that the observed frequency agrees perfectly with that calculated from the Nernst-Lindemann specific heat formula and less perfectly with the Debye "limiting frequency" for diamond. Ramaswamy also discussed the reason for the appearance of the rest-strahlen frequency as a Raman shift in diamond, as contrasted with its non-appearance in the alkali halides. Ramaswamy's claim that 1332 cm.$^{-1}$ is the fundamental vibration frequency of the diamond lattice has been fully confirmed by the theoretical work of Nagendra Nath (1934), Venkatarayudu (1938) and of Bhagavantam and Venkatarayudu (1939). Their investigations have made it clear that an oscillation of the two interpenetrating lattices of carbon atoms with respect to each other would have this frequency and that it would be active in the Raman effect.

Other experimental facts have however awaited a satisfactory explanation. Amongst these should be specially mentioned the observation by Bhagavantam (1930) of several other feeble lines in the Raman spectrum

of diamond with frequency shifts both larger and smaller than 1332 cm.$^{-1}$, the strongest of them having a frequency shift of 1158 cm.$^{-1}$ The significance of this observation as well as of the infra-red absorption data for diamond recorded by Julius, Angstrom, Reinkober (1911) and Robertson and Fox (1930) was far from being clear. To throw some light on these matters, Dr. Nagendra Nath (1937–40) made an elaborate investigation of the frequency spectrum of the diamond on the basis of the Born theory. His results however remained unpublished.

The subject entered on a new phase as the result of the investigations by P. G. N. Nayar (1941, 1942) of the luminescence and associated absorption spectra of diamond at liquid air temperatures. Nayar worked with some of the diamonds in the extensive collection made by Sir C. V. Raman, and his results showed conclusively that the lattice spectrum of diamond contains a whole series of *discrete* frequencies stretching from 1332 cm.$^{-1}$ downwards to quite low values. To explain these results of Nayar, Sir C. V. Raman (1941) put forward a new theory of the lattice vibrations in crystals, the basis of which was the postulate that these vibrations are *repetitive patterns in space*, the unit of the pattern having dimensions either identical with or an integral multiple of the dimensions of the lattice cell in the crystal. This idea has received a precise mathematical form and a dynamical justification in the introductory paper of the present symposium by Sir C. V. Raman. It is there shown that a super-cell whose dimensions are twice as great as those of a lattice cell is the space-unit of the repetition-pattern of the atomic vibrations properly so called, while vibrations whose repetitive units are of still larger dimensions fall in the category of elastic vibrations.

The various modes of atomic vibration possible in diamond on the basis of the Raman theory have already been derived and discussed in an earlier paper by the present author appearing in the symposium. It will now be shown how an expression for their frequencies may be derived on the basis of a scheme of force-constants similar to that employed by Nagendra Nath and others in their investigations.

2. *The Geometry of the Lattice*

To enable us to proceed we require a suitable notation for the atoms in the lattice and their displacements. The eight atoms in the unit cube have the following positions:

1	2	3	4	
$(0, 0, 0)$	$(0, \frac{1}{2}, \frac{1}{2})$	$(\frac{1}{2}, 0, \frac{1}{2})$	$(\frac{1}{2}, \frac{1}{2}, 0)$	
5	6	7	8	(1)
$(\frac{1}{4}, \frac{1}{4}, \frac{1}{4})$	$(\frac{1}{4}, \frac{3}{4}, \frac{3}{4})$	$(\frac{3}{4}, \frac{1}{4}, \frac{3}{4})$	$(\frac{3}{4}, \frac{3}{4}, \frac{1}{4})$	

Atoms 2, 3, 4 can be obtained by primitive translations from 1 and 6, 7, 8 likewise from 5. The rotational and reflexional symmetry of the lattice is represented by 48 operations of the octahedral group. There are actually only two non-equivalent atoms in the lattice, 1 and 5, and these may be regarded as representative of two lattice systems. Each atom of a system is surrounded tetrahedrally by four atoms of the opposite system. These are its nearest neighbours. The next nearest neighbours of an atom are twelve in number and they come from the same system. Four atoms of type 2, four of type 3, and four of type 4 are the next nearest neighbours of 1. As an illustration, we give here all the next nearest neighbours of atom 5. Let us introduce operations t_x, t_y, t_z for translations through $(a, 0, 0)$; $(0, a, 0)$; $(0, 0, a)$, a being the length of the edge of an 8-atom cell. By combining these operations we can form a set of operations t_x, t_y, t_z, t_yt_z, t_zt_x, t_xt_y and $t_xt_yt_z$, eight in number. These carry the 8-atom cell in fact into the 8 cells of a supercell containing 64 atoms. $\bar{t}_x$ will be a translation through an opposite direction, *i.e.*, through $(-a, 0, 0)$. The symbol $5\,(t_x)$ may be used to denote an atom obtainable from 5 by the translation t_x. Similar notation can be used to denote for 6, 7, 8, etc. With this notation, the twelve next nearest neighbours of the atom can be indicated below as

$$\begin{aligned} &6_1 = 6\,(\bar{t}_y\bar{t}_z);\ 6_2 = 6;\ 6_3 = 6\,(\bar{t}_y);\ 6_4 = 6\,(\bar{t}_z) \\ &7_1 = 7\,(t_z\bar{t}_x);\ 7_2 = 7\,(\bar{t}_x);\ 7_3 = 7;\ 7_4 = 7\,(\bar{t}_z) \\ &8_1 = 8\,(\bar{t}_x\bar{t}_y);\ 8_2 = 8\,(\bar{t}_x);\ 8_3 = 8\,(\bar{t}_y);\ 8_4 = 8. \end{aligned} \tag{2}$$

The notation 6_1, 7_2, 8_3, etc., is very convenient and has been borrowed from Dr. Nagendra Nath's unpublished work. We are now in a position to illustrate how the normal modes can be derived.

3. *The Equations of Motion*

It has been explained in another paper that in a normal mode, it is sufficient to know the displacements of one atom and the relative displacements of the other atoms. These displacements are known when the normal co-ordinate is known. Further, in a normal mode all the atoms move with the same frequency. It is therefore sufficient to consider the equation of motion of a single atom. The kinetic energy of atom 5 is $2T = m\,(\dot{x}_5^2 + \dot{y}_5^2 + \dot{z}_5^2)$, all co-ordinates being displacements from the equilibrium position and parallel to the cubic axes. Since the equations of motion involve the derivative of the potential energy function with respect to x_5, y_5, or z_5 it is enough if we consider terms of the potential energy involving these only. The energy function chosen in this case represents the valence forces, forces of angular distortion and interaction between the next nearest neighbours. Accordingly,

potential energy terms involving atom 5 can be represented as

$$2V = K\,(d_{15}^2 + d_{25}^2 + d_{35}^2 + d_{45}^2) + K_\alpha\,(\theta_{23}^2 + \theta_{31}^2 + \theta_{12}^2 + \theta_{14}^2 + \theta_{24}^2 + \theta_{34}^2) + K_\alpha \sum_{r=1}^{12} \phi_{r5}^2 + K'' \sum_{r=1}^{12} D_{r5}^2. \quad (3)$$

The summation in the last two terms runs over the next nearest neighbours of atom 5. d_{15} represents the variation in the distance 1–5 while D_{r5} is the variation in the distance between atom 5 and one of its nearest neighbours, the atom r. θ_{rs} denotes the variation in the angle subtended at 5 by the atom 'r' and 's'. ϕ_{r5} denotes the variation in angle subtended by the atom 'r' and 5 at the appropriate atom. In terms of cartesian co-ordinates, these are given by

$$d_{rs} = (x_r - x_s)\,\xi_{rs} + (y_r - y_s)\,\eta_{rs} + (z_r - z_s)\,\zeta_{rs} \quad (4)$$

and the same type of expressions for D_{rs}. Here ξ_{rs}, η_{rs}, ζ_{rs} are the direction cosines of the lines joining the 'r'th atom to the 's'th atom. If (a_r, b_r, c_r) and (a_s, b_s, c_s) are their positional co-ordinates, and l_{rs} the distance between them

$$\xi_{rs} = \frac{a_r - a_s}{l_{rs}},\ \eta_{rs} = \frac{b_r - b_s}{l_{rs}},\ \zeta_{rs} = \frac{c_r - c_s}{l_{rs}}. \quad (5)$$

We also have,

$$p\,\theta_{rs} = \sqrt{3}\,d_{rs} - \sqrt{2}\,(d_{rt} + d_{st}), \quad (6)$$

where p is the distance between nearest neighbours in equilibrium configuration and 't' denotes the suffix of the atom at which 'r' and 's' subtend the valence angle. Similar expressions hold for ϕ_{rs}. These relations enable us to write down the Hamiltonian in terms of cartesian co-ordinates and form the equations of motion. Differentiating the potential energy function and equating the rate of change of momentum to it, we get the following equation of motion for x_5.

$$\begin{aligned} -m\ddot{x}_5 = \lambda x_5 = {} & P x_5 - Q\,(x_1 + x_2 + x_3 + x_4) + S\,(x_{6_1} + x_{6_2} + x_{6_3} + x_{6_4}) \\ & - U\,(x_{7_1} + x_{7_2} + x_{7_3} + x_{7_4} + x_{8_1} + x_{8_2} + x_{8_3} + x_{8_4}) \\ & - R\,(y_1 - y_2 - y_3 + y_4 + z_1 - z_2 + z_3 - z_4) \\ & - V\,(y_{6_1} - y_{6_2} - y_{6_3} + y_{6_4} + z_{6_1} - z_{6_2} + z_{6_3} - z_{6_4}) \\ & + V\,(y_{7_1} - y_{7_2} - y_{7_3} + y_{7_4} + z_{8_1} - z_{8_2} + z_{8_3} - z_{8_4}) \\ & - U\,(y_{8_1} - y_{8_2} - y_{8_3} + y_{8_4} + z_{7_1} - z_{7_2} + z_{7_3} - z_{7_4}) \end{aligned} \quad (7)$$

where $\lambda = (2\pi\nu)^2 m$, m being the mass of the carbon atom and ν the frequency.

$$P = \tfrac{4}{3}\,(K + 7K_\alpha + 3K''),\ Q = \tfrac{1}{3}\,(K + 8K_\alpha),\ R = \tfrac{1}{3}\,(K - 4K_\alpha),$$
$$S = \frac{2K_\alpha}{3},\ U = \frac{K_\alpha}{6} + \frac{K''}{2},\ V = -\frac{K_\alpha}{3}. \quad (8)$$

4. *The Expressions for the Frequencies*

Once the equation of motion for x_5 is written out, we can substitute in it the known relative displacements of the other atoms in any chosen normal mode. The normal mode completely specifies the displacements of every atom in the cell in terms of x_5 and putting the values in (7) we get an expression for ν, the frequency. Among the normal modes we need pick out for consideration only eight, with only one each from a set of mutually equivalent degenerate modes. There are only eight such distinct *frequencies* and taking the cases one by one the expressions will be calculated. A knowledge of the normal co-ordinates is assumed here and can be easily taken over from earlier papers.

(1, 1, 1) *vector.* $\chi(t_x)=\chi(t_y)=\chi(t_z)=1$;

$$x_5=x_6=x_7=x_8=x_{5_1}=x_{5_2}=\text{etc.}, \quad =x_{8_1}=x_{8_2}=\text{etc.},$$
$$=-x_1=-x_2=-x_3=-x_4=\text{etc.}$$

as all the eight super-cells go the same way, with the lattice systems 1 and 5 going the opposite ways. The y and z displacements are zero; substituting these we get

$$\lambda_1=\frac{8K+64K_\alpha}{3m}: \qquad \text{Degeneracy 3.}$$

$(-1, -1, -1)$ *vector.*

$$\chi(t_x)=\chi(t_y)=\chi(t_z)=-1.$$

Therefore $-u_5=u_{6_1}=u_6=-u_{6_2}=-u_{6_4}=u_7=u_8$, etc.,
and correspondingly for u_1, u_2, etc. $u=x$, y, or z.
These relations hold for all frequencies of this vector.

λ_2 corresponds to the motion of alternate (1, 1, 1) planes normal to themselves.

Here $x_1=y_1=z_1=-x_5=-y_5=-z_5$
with the relative displacements of the other atoms defined as above. Substituting

$$\lambda_2=\frac{2K+8K''}{m}: \qquad \text{Degeneracy 4}$$

λ_3 is defined by $x_1=y_1=z_1=x_5=y_5=z_5$: Degeneracy 6

$$\lambda_3=\tfrac{2}{3m}(K+32K_\alpha+12K'')$$

λ_4 is defined by $z_1=-x_1=-z_5=x_5$: Degeneracy 8

$$\lambda_4=\frac{8K+34K_\alpha}{3m}+\frac{2K''}{m}$$

λ_5 is defined by $z_1=-x_1=z_5=-x_5$: Degeneracy 8

$$\lambda_5=\frac{6K_\alpha+2K''}{m}.$$

In these modes the relative displacements of all the atoms equivalent to 1 or 5 must be derived from the characteristic relations defined by the vector (1, 1, 1). On substituting all these, the expressions given above are obtained.

(1, − 1, − 1) *vector*

λ_6 defined by $x_5 = x_6 = -x_7 = -x_8$

$$\lambda_6 = \frac{4K + 40K_\alpha}{3m} + \frac{8K''}{m} : \qquad \text{Degeneracy 6.}$$

The motion of the rest of the atoms is defined by the above vector.

For λ_7 and λ_8 involving motions in tangential directions there is no displacements of the x co-ordinate so far as this vector is concerned. Since we have written down the equation for x_5, it is convenient to consider the (− 1, 1, − 1) or (− 1, − 1, 1) vectors for λ_7 and λ_8.

$z_1 = -z_2 = z_3 = -z_4 = x_5 = -x_6 = x_7 = -x_8$

and $z_1 = -z_2 = z_3 = -z_4 = -x_5 = x_6 = -x_7 = x_8$

define the two modes for (− 1, 1, − 1) vector. Substituting these relations, we get

$$\lambda_7 = \frac{12K_\alpha + 4K''}{m} \quad : \qquad \text{Degeneracy 6}$$

$$\lambda_8 = \frac{8K + 4K_\alpha}{3m} + \frac{4K''}{m} \quad : \qquad \text{Degeneracy 6}$$

This completes all the 8 frequencies. We finally present in a tabular form all the 8 frequencies with their degeneracies.

Frequency Number	Description	Magnitude	Degeneracy
λ_1	Two lattices moving oppositely	$\frac{8K + 64K_\alpha}{3m}$	3
λ_2	Motion of alternate sets of octahedral planes as fully explained in earlier papers	$\frac{2K + 8K''}{m}$	4
λ_3		$\frac{2}{3m}(K + 32K_\alpha + 12K'')$	4
λ_4		$\frac{8K + 34K_\alpha}{3m} + \frac{2K''}{m}$	8
λ_5		$\frac{6K_\alpha + 2K''}{m}$	8
λ_6	Motion of alternate cubic planes as explained in earlier papers	$\frac{4K + 40K_\alpha}{3m} + \frac{8K''}{m}$	6
λ_7		$\frac{12K_\alpha + 4K''}{m}$	6
λ_8		$\frac{8K + 4K_\alpha}{3m} + \frac{4K''}{m}$	6

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Summary

The eight frequencies in a diamond lattice are calculated with a suitable force field and explicit expressions are given for them. Sir C. V. Raman's theory of superlattice vibrations is the basis of the investigation.

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MODES OF VIBRATION OF THE HEXAGONAL CLOSE-PACKED LATTICE

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1. *Introduction*

The hexagonal close-packed structure is a frequently encountered atomic arrangement in the crystalline form of many metallic elements. It is associated with a hexagonal unit cell having the axial ratio c/a equal to 1·63, and is a closest packing of spheres. The unit cell contains two atoms which have the co-ordinates 0, 0, 0; 2/3, 1/3, 1/2. In some metals, the axial ratio is slightly different from 1·63, but the co-ordinates of the atoms is the same. In this paper, the modes of vibration of the hexagonal close-packed structure are investigated on the basis of the fundamental ideas proposed by Sir C. V. Raman in an earlier paper. The results are true for any hexagonal structure in which there are atoms at 0, 0, 0; 2/3, 1/3, 1/2 and is not restricted to the case where the axial ratio is 1·63.

In a preceding paper, the author has discussed the modes of vibration of a simple hexagonal Bravais lattice, and has shown that the eight types of vibration fall into four sets, namely $(+\,+\,+)$; $(+\,+\,-)$; $(+\,-\,+,\ -\,+\,+,\ -\,-\,+)$; $(+\,-\,-,\ -\,+\,-,\ -\,-\,-)$. We shall now take up each of these sets, and discuss the modes of the close-packed lattice under it, using group theoretical methods. In this connection, it must be noted that the crystal belongs to the space-group D^4_{6h}, in which the inversion is not at a lattice point, but is at a point midway between the two atoms, *i.e.*, at 1/3, 1/6, 1/4. Hence, the method used by E. V. Chelam in an earlier paper in discussing the vibration of the diamond lattice is employed for deriving the character table and the modes of vibration.

2. *The* $(+\,+\,+)$ *and* $(+\,+\,-)$ *Types of Vibration*

We first consider the two atoms in the unit cell to be different, so that there is no centre of inversion. Then, the group of the vibration (*cf.* earlier paper by the author) is $D_{3\bar{h}}$, whose character table is drawn up below. The reduced character $\psi(R)$ for each of the operations in the $+\,+\,+$ type is tabulated below against ψ_{+++}. Thus, two vibrations (coupled) are

obtained under A_2'' and two others coupled under E'. On introducing the centre of inversion, the coupling is removed, the modes splitting up into two, symmetric and antisymmetric with respect to inversion. Also, it is easily seen that these modes are distinct. They represent the three translations of the lattice as a whole, and three vibrations of the two interpenetrating lattices against one another, one being along the hexagonal axis and the other two degenerate in the perpendicular plane.

D_{3h}	E	σ_h	$2C_3$	$2S_3$	$3C_2$	$3\sigma_v$	n_i (+ + +)	n_i (+ + −)
A_1'	1	1	1	1	1	1	..	1
A_2'	1	1	1	1	−1	−1	..	..
A_1''	1	−1	1	−1	1	−1	..	..
A_2''	1	−1	1	−1	−1	1	2	1
E'	2	2	−1	−1	0	0	2	1
E''	2	−2	−1	1	0	0	..	1
ψ_{+++}	6	2	0	−4	−2	2		
ψ_{++-}	6	0	0	0	0	2		

Coming to the + + − type of vibration, it has been shown by the author (*loc. cit.*) that for the simple hexagonal lattice, the group of the vibration is D_{6h}. In the present case, if we consider the two atoms to be distinct, there is no centre of inversion, and the group is only D_{3h}, which is the same as for + + +. The reduced character for this is tabulated in the character table against ψ_{++-} and the number of modes n_i under each state is determined. It is found that there is one mode each under A_1', A_2'', E' and E''. On introducing the centre of symmetry, and associating it with the operations of the group D_{3h}, the translation operators are brought in thus:

$$i\sigma_h i^{-1} = \sigma_h \tau_z;\ iC_3 i^{-1} = C_3 \tau_x;\ iS_3 i^{-1} = S_3 \tau_x \tau_z;\ iC_2 i^{-1} = C_2 \tau_x \tau_z;\ i\sigma_v i^{-1} = \sigma_v \tau_x.$$

Hence, the operations of D_{3h} do not commute with the inversion, and the group $D_{3h} \times i$ contains the product of the operations of D_{3h} and the translations. It has been shown by Chelam (*loc. cit.*) that the character of the product of an operation R of the point-group and a translation T is the product of their characters, *i.e.*, $\chi(RT) = \chi(R)\,\chi(T)$. Thus, on introducing the inversion, the following transformations occur:

$\chi(\sigma_h) \rightarrow -\chi(\sigma_h)$; $\chi(C_3) \rightarrow \chi(C_3)$; $\chi(S_3) \rightarrow -\chi(S_3)$; $\chi(C_2) \rightarrow -\chi(C_2)$ and $\chi(\sigma_v) \rightarrow \chi(\sigma_v)$. Hence, the representations A_1' and A_2'' are sent one into the other and so are E' and E''. Thus these are equivalent under the inversion and give rise respectively to a double and a quadruple representation in the space-group. Thus, the vibrations symmetric and antisymmetric

with respect to the inversion are identical. Hence, under this type, we have a vibration along the hexagonal axis with degeneracy 2, and another degenerate in the perpendicular plane with degeneracy 4.

3. The Remaining Types of Vibration

The vibration represented by the set $(+ - +, - + +, - - +)$ denotes the vibration of atoms in alternate prismatic planes. Taking one of them, $+ - +$, it is easily seen that the group of the vibration is only C_{2v}, if the two atoms are considered distinct. The character table is given below. The transformations on introducing the inversion are $iC_2i^{-1} = C_2\tau_x\tau_z$; $i\sigma_v i^{-1} = \sigma_v\tau_x$; $i\sigma_v' i^{-1} = \sigma_v'\tau_z$. These keep the representations invariant, so that each of them splits into two, one symmetric and the other antisymmetric, with respect to the inversion. In these, the successive atomic planes have the phases $+ - - +$ and $+ + - -$ respectively. These are distinct since the planes are not equally spaced.

C_{2v}	E	C_2	σ_v	σ_v'	n_i $(+ - +)$	n_i $(+ - -)$
A_1	1	1	1	1	2	2
B_2	1	−1	−1	1	2	1
A_2	1	1	−1	−1	..	1
B_1	1	−1	1	−1	2	2
$\psi + - +$	6	−2	2	2		
$\psi + - -$	6	0	2	0		

The last set $(+ - -, - + -, - - -)$ represents vibrations of atoms in diagonal planes of the type $(01\bar{1}1)$. For this also, the group of the vibration is C_{2v} and taking one of the types, $+ - -$, the values of ψ and n_i are shown in the above character table. Using the transformations in the previous paragraph, it is seen that the representations A_2 and B_2 become equivalent, and so do A_1 and B_1. Thus, we get a doubly degenerate vibration antisymmetric to σ_v, and two coupled doubly degenerate vibrations symmetric to it. The direction of the former is parallel to the plane and perpendicular to the hexagonal axis. It may also be described as the intersection of the vibrating plane with the horizontal reflection plane of the lattice. The other two vibrations take place in two unspecifiable directions in the perpendicular plane σ_v. A physical explanation for the equivalence of the symmetrical and antisymmetrical modes consists in the fact that the vibrating planes may be imagined to be either the $(01\bar{1}1)$ or the $(01\bar{1}\bar{1})$ planes.

The modes of vibration may thus be described as follows:—

No.	α β γ	*Description*	*Number of modes*
1, 2	+ + +	Translation of the lattice as a whole	1, 2
3	+ + +	Vibration of the atoms in the two lattices against each other, in a direction parallel to the hexagonal axis Oz	1
4	+ + +	Same as (3), but in a plane perpendicular to Oz, the vibration being degenerate in the plane	2
5	+ + −	Vibration of basal (0001) planes with the phases (+ + − −) and (+ − − +) normally	2
6	+ + −	Same as (5), but transversely degenerate in the plane ..	4
7 to 9	+ − + − + + − − +	Vibrations of prismatic planes in three directions, normally, transversely perpendicular to the hexagonal axis, and parallel to it, with the phases + + − −	3, 3, 3
10 to 12	do	Same as (7) to (9) but with the phases + − − + ..	3, 3, 3
13	+ − − − + − − − −	Vibration of the $(01\bar{1}1)$, $(10\bar{1}1)$, $(1\bar{1}01)$ planes with the phases (+ + − −) and (+ − − +) in a direction in the plane perpendicular to the hexagonal axis	6
14, 15	do	Same as (13), but in two unspecifiable directions in a plane perpendicular to the direction in (13), as described above	6, 6
		Total ..	48
		Number of distinct modes ..	13

In conclusion, I wish to express my grateful thanks to Prof. Sir C. V. Raman for the keen interest that he took in the investigation.

Summary

The modes of vibration of the hexagonal close-packed structure is worked out on the basis of the Raman theory of crystal vibrations. The character tables are drawn up, and the vibrations are derived by a method due to E. V. Chelam without using the character table of the space-group. It is found that there are 13 vibrations with degeneracies 1, 2, 2, 4, 3, 3, 3, 3, 3, 6, 6, 6. The planes which take part in each mode and the directions of vibration for these are also described.

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